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**VOLUME X**

**1933**



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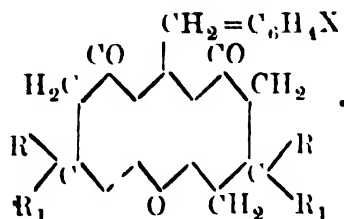
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# ERRATA.

Page.	Line.	Read	For
8	11	Molecule hy-	Molecule hy'
9	4	elucidation	illucidation
13	15	<i>Insert</i> 'are' between 'solvents' and 'so'	
16	15	<i>Read</i> Challong-	Challange
24	15	21	2
	39	J. B. Biot	J. C. Biot
25	2	25	5
	6	Landau	Landu
	7	1908	19 8
	20	vii	viii
	29	1930	1933
	35	<i>J. Chem. Soc.</i>	<i>Chem. Soc.</i>
	42	L. Pasteur	M. Pasteur
	45	Spencer	Spenser
		59	52
26	5	Braun	Braum
	8	<i>Insert</i> '60' before 'See'	
205	13*	<i>Read</i> acids* (The fat from which these acids were obtained was standing in the lab. for over a year)	acids
210	3*&4*	as 95.5 (Arnaud and Posternak, <i>Compt. rend.</i> , 1910, <b>150</b> , 1130) and as 95 (Hilditch, <i>J. C. S.</i> , 1926, 1829)	and also as 95.5 (Arnaud and Posternak, <i>Compt. rend.</i> , 1910, <b>150</b> , 130)
	5*&7*	dihydroxystearidic acid	dihydroxystearic
396	4	when 75%	when contain 75%
396	4*	for elaidic ( <i>iso</i> oleic) acid and methyl oleate	for elaidic ( <i>iso</i> oleic) methy oleate
	4*	elaidate	elaidale

664 top *Read* the formula as



\* From bottom



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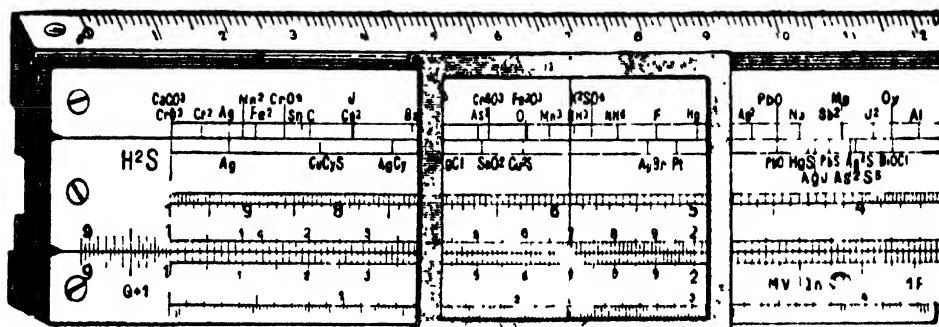
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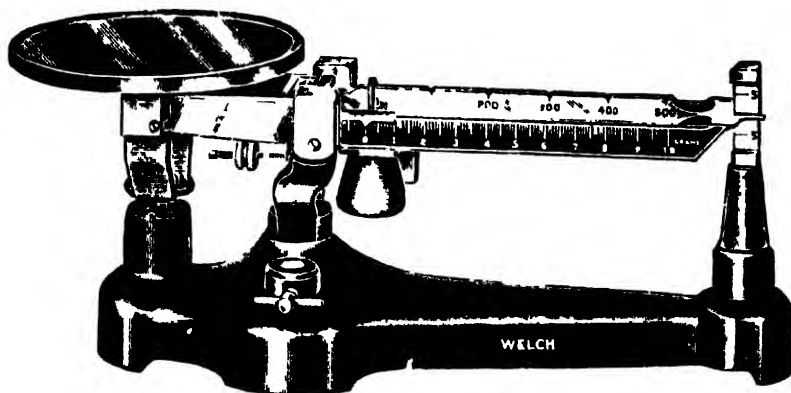
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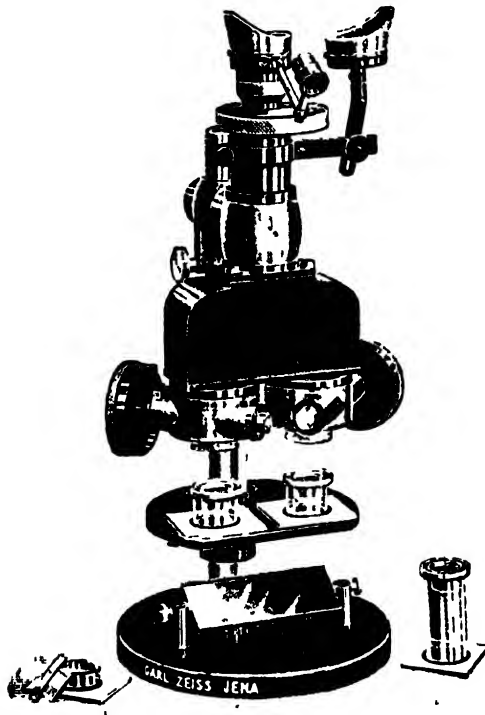


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## **I. The Indian Chemical Society (1924-1932).**

## **II. The Science of Optics in the Service of Chemistry\***

**BY BAWA KARTAR SINGH, M.A., Sc.D., F.I.C.**

In my last presidential address at Bangalore, I pointed out that the custom had grown which required the President to give his address on some purely scientific subject. At this anniversary meeting, I propose to make a slight departure from this practice, and to give some account of the Society as "a body politic and corporate."

I shall, therefore, divide my address into two parts. The first of these will deal with the life of the Society during the nine years of its existence. This will enable our Fellows to take stock of the progress which has been achieved since the foundation of the Society in 1924. The second part of my address will describe the services which the Science of Optics has rendered to chemistry and will contain brief comments on studies on the rotatory dispersion of organic compounds carried out at Ravenshaw College, Cuttack.

### **I. THE INDIAN CHEMICAL SOCIETY (1924-1932).**

The Indian Chemical Society came into existence in 1924 as the result of several meetings and deliberations of chemists held at Madras (1922), Lucknow (1923) and Bangalore (1924), during the Science Congress Weeks. This gave it, from the very commencement, an All-India character, which was further guaranteed by requiring its anniversary meeting to be held in conjunction with the annual gathering of the Indian Science Congress. The latter is a peripatetic body and holds its meeting at different centres of learning. In this way it was hoped to establish personal contact between the Society and its Fellows, scattered all over India.

The Indian Chemical Society was registered as a corporate body on the 9th May, 1924. The first meeting of the Council was held on

\* Presidential address delivered at the Ninth Annual General Meeting of the Indian Chemical Society, held on the 3rd January, 1933 at Patna.

the 30th September, 1924, and the first ordinary meeting on the 24th November, 1924. Thus the Society now enters the tenth year of its existence. During this period it has made steady progress in the number of its Fellows and subscribers, in the number of exchange journals, in the size of its own journal and in its general financial condition. The progress achieved under these different heads can be judged from the figures given in Tables I and II.

TABLE I.

*Table showing the progress of the Society during 1924-1932.*

Year.	No. of Fellows.	No. of Subscribers.	No. of Exchange Journals.	No. of Pages published.	No. of Papers received.	No. of Papers Published.
1924	101	15	10	224	33	23
1925	213	61	38	449	45	44
1926	339	78	45	430	71	48
1927	340	81	54	572	75	78
1928	348	87	84	778	109	88
1929	393	98	93	1014	143	106
1930	377	102	103	950	115	113
1931	387	105	110	794	110	100
1932	360	100	116	700	111	98

The number of Fellows, which was 101 in 1924, increased in 1929 to the record figure of 393, but it fell to 360 in 1932. The number of subscribers to the journal shows a steady increase which reflects the popularity of the journal. The Society has instituted a Free list by which the journal is sent free of cost to 108 institutions. It was decided last year to raise this number to 158. The number of exchange journals now reaches the high figure of 116. In these ways it is sufficiently ensured that the original papers published in our journal get wide circulation. The size of the journal has also increased. In 1924, the number of pages printed was 224; it increased to 1014 in 1929. But owing to financial difficulties, it has not been possible to maintain the same size. On the other hand, the Society has been forced to keep it within the sanctioned limit of 750 pages, which are printed free of cost by the University of Calcutta.

The development of the journal is thus being retarded with obvious detriment to the progress of chemistry in this country. It is, however, hoped that the Society will be able to devise means to overcome these obstacles to its progress.

During the first four years of its existence (1924-27), the journal was quarterly. It was made bi-monthly during 1928-29. Since 1930, it has become a monthly publication. The change has had one beneficial result; it takes much less time now for a paper to appear than formerly.

The financial position of the Society during the period under review is shown in a tabular form, under summary of accounts (Table II).

TABLE II.

*Summary of Accounts for 1924-1932.*

Year.	Total Re- ceipts.	Subscriptions from Fell. Subs- cowers. cribers.		Sale proceeds.	Adver- tisement proceeds.	Dona- tions.	Expen- diture.	Balance.	Reserve Fund.*
	Rs.	Rs.	Rs.	Rs.	Rs.	Rs.	Rs.	Rs.	Rs.
1924	3,120	2,085	nil	78	50	300	1,302	1,818	nil
1925	8,075	3,005	1,084	378	512	3,045	2,607	5,468	4,500
1926	6,136	4,260	1,273	151	451	3,200	1,687	1,449	9,696
1927	7,927	4,607	979	98	509	1,600	5,913	2,014	9,696
1928	9,726	4,512	1,433	329	621	2,650	7,252	2,474	13,870
1929	10,980	5,714	1,491	419	654	2,400	8,415	2,574	15,900
1930	9,037	4,742	1,450	271	716	1,400	9,511	2,430	16,400
1931	10,534	5,352	1,500	439	1,072	1,500	9,515	2,495	19,814
1932	10,932	4,953	1,428	490	1,063	1,375	8,725	3,207	21,213

Although the expenditure of the Society has increased from Rs. 1302 in 1924 to Rs. 8415 in 1929, there has been a corresponding rise in the income of the Society during the same period. In spite of the fact that the year 1930 showed an opening balance of Rs. 2,574, the financial position of the Society

\* The Special Reserve Fund of Rs. 10,000 for a Building of the Indian Chemical Society is not included in this column.

suffered a set back this year owing to the large arrears in subscriptions from Fellows, smaller number of new admissions, and a fall in the amount received from donations. This must be attributed to the general economic depression in world trade. Scientific societies in other countries have also been similarly hard hit. Another reason for an adverse balance in the income and expenditure of the Society in 1930 was that owing to the increase in the size of the journal in 1929, a large sum had to be paid to the University of Calcutta for printing 264 pages in excess of the sanctioned limit. Consequently the size of the journal has been reduced since 1931. Another unfortunate effect of this adverse state of affairs has been the discontinuance of the research grant since 1930. As a result of these drastic steps, the position of the Society has been again rendered solvent. The reserve fund shows a balance of Rs. 21,243, there being also a special fund of Rs. 10,000 for a building for the Chemical Society.

#### *Building for the Indian Chemical Society.*

Since its inception, the Indian Chemical Society has been housed in the Science College, University of Calcutta, usually in the private room of the Honorary Secretary, who has always happened to be a Professor of this institution. With each change in the Secretary, the Society has had to shift itself from room to room. At present the office is located in one corner of the library of the Chemical Department, and is allotted a space measuring only about 12' x 10'. The office is overcongested. The valuable exchange journals are stored away, and cannot, therefore, be consulted by our Fellows. This arrangement, which is very unsatisfactory, is only of a temporary nature and may be terminated at any time, should the needs of the Science College demand such a step. The Council of the Society has always kept itself busy in finding out a solution of this urgent problem. Our First President, Sir P. C. Rây, made a generous gift of Rs. 10,350 towards the Building Fund in 1932, and several attempts were made by the Council to secure a home for the Society. The Government of Bengal were moved to grant a lump sum towards the cost of the building, the plan and estimate of cost, asked for by Government, being duly submitted by

us. But owing to their financial difficulties, the Government of Bengal did not find themselves in a position to help us.

The Corporation of Calcutta was also approached with a view to obtain a suitable plot in the proximity of the Science College or the Presidency College, but we were informed that no such site was available. In connection with these attempts of the Council to secure a home for the Society, I should specially mention Dr. J. N. Mukherjee for his tireless efforts on our behalf. The Council of the Society made another attempt in September, 1932, towards securing a home for itself in negotiations which are still pending with the University of Calcutta. If this scheme fructifies, the University will complete the third storey of the extension of the southern wing of the Science College at an approximate cost of Rs. 10,000 and the Society will pay this sum from its Building Fund to the University on condition that in case the rooms were required by the University for its own purposes, this sum will be returned to the Indian Chemical Society. I would recommend the scheme for your warm approval, for in that case the Society will get three large rooms with a floor area of 1740 square feet, which will be sufficient for its needs for some time to come. One great advantage of the scheme is that the overhead charges for maintenance and service of these rooms would be very small.

#### *The Council of the Indian Chemical Society.*

Last year the number of ordinary members of the Council was raised to 20. The method of election to the Council and distribution of these seats among the different territorial centres of active chemical research was entrusted to a sub-committee, the report of which will be considered at this annual meeting.

#### *Branches of the Indian Chemical Society.*

On account of the great distance of active centres of chemical research from Calcutta, the headquarters of the Society, it is not usually possible for Fellows from these centres to attend more than one meeting annually, namely, the anniversary meeting, which is held in the first week of January, in conjunction with the gathering of the Indian Science Congress. For this reason

any centre of learning with forty Fellows on the rolls of the Society is entitled to the privilege of forming a branch Society. The parent Society remits 10 per cent of the subscriptions to the branch Society for its expenses. The branch Society in return submits its annual report together with a statement of accounts to the Indian Chemical Society. We have now three such branches at Lahore (7th December, 1925), Bombay (29th April, 1926) and Madras (27th March, 1929). The Lahore branch has been most successful in raising funds for several post-graduate research scholarships. Another interesting feature of this branch is its annual dinner—a very important social function—thus setting a great example in social life to the parent Society. The credit for this, among others, goes to my esteemed colleague, friend and old pupil, Dr. S. S. Bhatnagar.

*Sir. P. C. Rây Jubilee Celebration.*

The great Indian Savant and benefactor of the Society, Sir P. C. Rây attained his 70th birthday last year. The Council of the Society decided to celebrate this auspicious occasion by publishing a commemoration volume, containing original papers, or resumés of original work. This volume, together with an address from the Council, will be presented to Sir P. C. Rây on your behalf, as a token of the high esteem and love in which he is held by all of us.

*Honorary Fellows.*

The first honorary fellowship of the Society was conferred in 1929 on Prof. A. Sommerfeld of Munich, at the time of his visit to Calcutta in 1928-29. This year the same honour is to be conferred on Sir C. V. Raman, whose nomination has been unanimously recommended by the Council. I need hardly refer to the unique scientific attainments of Sir C. V. Raman which are so well known to all of you, and the outstanding distinction conferred on him by the award of the Nobel Prize for Physics for 1930, for his researches on light-scattering, which led to the discovery of the "Rathan Effect," must be still fresh in your mind.

*Our Requirements.*

The most urgent need of the Society is money for removing our two long-felt wants. One of them relates to the permanent housing

of the Society, to which reference has already been made. The second is the provision of a whole time paid Editor of the Journal. He should possess at least the qualifications of a University Reader with sufficient emoluments to attract the best man. As time goes on, and the journal increases in size, the services of such an Editor will become almost indispensable to its efficient editing and management. I would, therefore, appeal, through you, to people of wealth to come forward with liberal contributions and endowments for these purposes.

## II. THE SCIENCE OF OPTICS IN THE SERVICE OF CHEMISTRY.

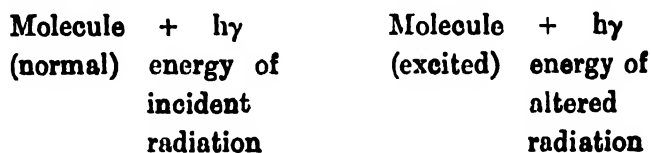
I now pass on to the second part of my address. The Science of Optics has had a very intimate connection with Chemistry and its applications have rendered signal service to the growth of chemical theory. Refraction, absorption, and optical activity, both natural and magnetic, have been studied by the chemist for over a century.

### *Raman Effect and Infra-red Absorption.*

Recently the study of light-scattering has proved of fundamental importance to the science of chemistry. This phenomenon was first observed in 1923 by Dr. Ramanathan\*, working under Sir C. V. Raman<sup>1</sup> at Calcutta. When an optical medium (such as a gas, liquid, crystal or glassy solid) is illuminated with monochromatic light, much of the most intense part of the spectrum of the internally scattered light emerging from within the volume of the

As early as 1923, Ramanathan while working on the scattering of light in liquids, noticed that there is a feeble radiation emitted by even the most carefully purified liquids, the wave-length of which is not the same as that of the incident light. This was at first mistaken for fluorescence, but it was difficult to understand why almost all liquids should persist in showing it, even after repeated purification which should remove all the fluorescent impurities. Ramanathan, therefore, described it as 'a special kind of feeble fluorescence'. It is now known that this peculiar radiation is only an aggregate effect of the well-known line spectrum discovered by Sir C. V. Raman in 1928. The chief drawback in the earlier work (1923) was that a spectroscope was not made use of, and the visual observations could not reveal the existence of any discrete wave-lengths. In addition to these observations of Ramanathan, and prior to the discovery of the Raman Effect in 1928, there are numerous references to this phenomenon in several papers by Raman and his co-workers.

substance is a line in the same position as for the incident light. Along with this we have radiations of altered frequency consisting partly of new lines or bands displaced from the parent line and also, in the case of fluids, of a continuous spectrum which envelops both the parent line and the new or displaced lines appearing in the spectrum. The Raman Spectrum thus obtained is characteristic of the substance used, and moves bodily up or down the scale of frequency, when the frequency of the incident radiation is varied. It may be represented by a reversible energy-reaction between matter and radiation according to the scheme.



The scattering process involves, in general, an exchange of energy between the light quantum or photon and the molecules. If the photon loses part of its energy to the molecule, it would be scattered with a diminished frequency; on the other hand if the photon gains energy from the molecule, it is scattered with an increase of frequency.

The essential features of the Raman Effect are (a) its universality—it is observed in gases, liquids, crystals or glassy solids; (b) its spectral character; (c) its representation as interaction between matter and radiation. The frequency difference between the incident radiation and the Raman Line is independent of the wave-length of the exciting radiation, and coincides in magnitude with the infra-red absorption frequency of the molecule. In this way, Raman Effect is correlated with the infra-red absorption spectra of chemical substances, and its utility as an aid to the exploration of molecular spectra, especially in the infra-red, is obvious. It is therefore, of great value in elucidating the shape, size and structure of molecules. The method of light scattering is, however, much more convenient and accurate to work with than the study of infra-red absorption with its experimental technique which is particularly difficult. The remote regions of the infra-red spectrum which are very difficult of access are made easily accessible by the Raman method. Certain inactive frequencies, not occurring in the infra-red absorption, appear very strongly in the Raman Spectrum. On the other hand, the fundamental modes of vibration of the molecule, which appear strongly



in the infra-red absorption may be extremely weak in scattering. There are thus very significant differences in the character of the two spectra. A combined study by the two methods is of the greatest importance for the elucidation of chemical constitution. The results obtained from a study of the Raman Spectrum can distinguish the nature of chemical binding, namely co-valent or electrovalent molecules. Electrovalent molecules give no lines, whereas co-valent molecules give strong Raman Lines<sup>2</sup>. Accordingly compounds which give the strongest spectra in light scattering are those of carbon—the typical co-valent element.<sup>2a</sup>

As the presence of non-ionised co-valent molecules in solution can be detected from a knowledge of the Raman Spectra, its utility in the study of electrolytic dissociation is also clear.<sup>2b</sup> One of the many other interesting results arising out of the application of the Raman Spectrum is the detection of the non-homogeneity of hydrogen.<sup>3</sup> The Raman Spectrum of liquid hydrogen indicates that this substance is a mixture of two effectively distinct set of molecules, which is in agreement with the result already obtained from measurements of the specific heat of hydrogen gas.<sup>3a</sup>

Raman Spectra being the most recent discovery in point of time, have been treated first, as they promise to provide more accurate knowledge of the structure of molecules than any other spectral method. A large amount of work is now being carried out in associating the shift of particular linkages, and as a result of this work much light is likely to be thrown on constitutive problems of complex organic compounds.

#### *Emission and Absorption Spectra in the Visible and Ultraviolet Regions.*

During the early days of spectroscopic work, the interest of the chemist lay chiefly in the assignment of many new spectra to elements and the compounds responsible for them. This was due to the pioneer investigations of Bunsen and Kirchoff, and led to important chemical discoveries, and in particular to the recognition of new elements. With improvements in experimental technique, such as the introduction of high dispersion spectroscopes, interferometers, etc., wave-length measurements were carried out more accurately, and by the year 1918, about 100,000 lines had thus been registered. Spectroscopic analysis is proving an invaluable aid to chemical analysis. On the qualitative side, its utility lies in its rapidity and

certainty. Its remarkable sensitivity is well illustrated by A. de Gramont's observation that zinc is a constituent of all animal organisms<sup>4</sup>. In qualitative spectroscopic analysis, the material to be examined is introduced into an arc or into a condensed spark<sup>5</sup>, and the spectrum is photographed with a quartz spectrograph over the wave-length range, 7,000—2,000Å. A comparison spectrum, such as that of the iron arc, is cast upon the same plate. The wave-lengths of the lines from the unknown material are measured by means of a micrometer, and are identified with known spectra by reference to standard Tables of wave-lengths<sup>6</sup>.

Applications of spectroscopic observations to quantitative analysis depend on indirect methods. The method of N. Lockyer<sup>7</sup> is based on a comparison of the length of lines from an unknown material with the length of the same lines from a series of standards of known composition. The method of W. N. Hartley is based on his discovery (1884) that if the quantity of any element present in a material is gradually diminished to a very small value, lines due to that element successively disappear from the resulting spectrum until only a few are left. The first method is cumbersome, and the second is semi-quantitative. There is, however, a third method developed by de Gramont<sup>8</sup> and by Meggers, Kiess, and Stimson,<sup>9</sup> which is the most satisfactory. It utilises the intensity of the lines of the elements as a spectroscopic quantity which varies in a determinable manner with its quantity present in the sample under examination. The intensities of the lines in a spectrogram from the material are compared and matched with their intensities in a series of spectrograms taken under the same conditions from material of known composition. The spectrograms in both cases are obtained by introducing the materials as the poles of a condensed-spark apparatus, and photographing their spectra under the same conditions. The success of this method depends on the use of a standard form of apparatus, constant observing conditions, and the careful preparation of a series of comparison samples. These spectroscopic methods have great attraction for the chemist, as they surpass ordinary gravimetric methods in rapidity and precision, when dealing with abnormally small quantities of material. Numerous applications of this method have already been made, such as, the quantitative analysis of steels.<sup>10</sup> Spectroscopic methods have also found application in industrial uses, as for example, the determination of nickel in fats.<sup>11</sup>

Complex molecules which give characteristic absorption spectra have also been brought within the scope of the spectroscope by utilising the same principle as that employed for emission spectra by de Gramont, *i.e.*, comparison with a series of standards. The introduction of the spectrophotometer has, however, rendered unnecessary this tedious preparation of standards.

Ever since the pioneer investigations of Hartley and Huntingdon in 1879 on the spectra of liquids and solutions, absorption curves have been widely used in elucidating the structure of organic compounds.<sup>12</sup> Latterly these investigations have been made for the solutions of the problems of valency. From a careful study of the absorption spectra of an acid, its salt and its ester, it is shown that the ionic bond in salts gives a different spectrum from that of the non-ionic bond of the ester.<sup>12a</sup>

### *The Optical Rotatory Dispersion.*<sup>13</sup>

The phenomenon of rotatory polarisation depends on the property which certain substances possess of taking a beam of plane polarised light, and imparting a twist to the plane of polarisation: the plane polarised beam of light enters with all its vibrations compressed, say, in a vertical plane; it emerges with its vibrations which are no longer vertical, but are inclined to the right or to the left. The phenomenon of optical activity was discovered by Arago<sup>14</sup> in 1811 in the case of quartz, by Biot<sup>15</sup> in 1815 in the case of organic compounds, and by Faraday<sup>16</sup> in 1846 in the case of substances subjected to the influence of a magnetic field. The importance of this discovery to the chemist has been far reaching. Biot's pioneer work on the optical activity of organic compounds led to the discovery of molecular dissymmetry by Pasteur, and the theory of molecular dissymmetry in its turn has proved of immense value in the elucidation of molecular structure of chemical compounds. In this way, the services rendered by the polarimeter have been as notable as the results obtained with the help of the spectroscope.

Soon after the discovery of the phenomenon of rotatory polarisation, the first attempt to determine the mathematical form of the curves of the rotatory dispersion of quartz was made in 1817 by Biot,<sup>17</sup> who showed that the rotatory power was inversely proportional to the square of the wave-length, so that  $\alpha = k/\lambda^2$  or  $\alpha\lambda^2 = \text{constant}$ . This equation was verified by plotting the thickness of quartz required to produce a rotation of 90°, 180°, 270°, etc.,

against the square of the wave-length of the light. It is noteworthy that Biot arrived at this Law of Inverse Squares, inspite of the fact that he had no source of monochromatic light, and that his only wave-lengths were Newton's values. Notwithstanding the poor facilities in experimental technique available at that time, Biot always included measurements of rotatory dispersion in his work on optically active substances. He further proceeded to apply this law to those liquids in which he had also discovered the property of optical activity, *e.g.*, oil of turpentine and an aqueous solution of cane sugar. The method adopted was to balance the rotation of the liquid against that of a quartz plate of opposite sign. In each case the compensation appeared to be exact, which proves that the law of inverse squares held equally for the liquids as for the rock crystal. It was not, however, long before it was recognised that the law of inverse squares was not exact and universally true. Biot himself from the first had suspected small deviations; in 1836 he obtained definite evidence of this fact when trying to compensate *laevo*-rotatory turpentine against a *dextro*-rotatory oil of lemon, either in separate tubes, or mixed, and was led to observe that 'the compensation of the deviations, although very close for all the rays, was, however, neither complete nor general'<sup>18</sup>. Even the approximation to Biot's law, which had been found to hold good for all substances hitherto studied, disappeared in the case of aqueous solutions of tartaric acid. They were found to obey a totally different law, since the rotatory power of the acid, instead of increasing progressively as the wave-length of the light diminished, passed through a maximum in the green region of the spectrum.<sup>19</sup> Biot was thus led to divide optically active substances into two groups: (i) those which obeyed approximately the law of inverse squares, (ii) those which did not obey it, *e.g.*, tartaric acid. After Biot's death, on account of increased accuracy in polarimetric work, deviations from the law of inverse squares became too marked to be ignored, and led to its general abandonment even as a first approximation. Several other formulæ were, however, put forward as expressions connecting rotatory power with wave-length, such as those by von Lang and Stefan,<sup>20</sup>  $\alpha = A + B/\lambda^2$ ; by Boltzmann<sup>21</sup>,  $\alpha = A/\lambda^2 + B/\lambda^4$ , and by Lommel<sup>22</sup>,  $\alpha = k\lambda^2/(\lambda^2 - \lambda_0^2)^2$ . These formulæ, being empirical, proved of little value and broke down under more stringent experimental conditions. As a result of this, interest in the study of rotatory dispersion diminished. The dis-

covery of the Bunsen burner in 1866 made it easy to produce the D-line of the sodium flame which acquired almost a monopoly as a source of light for polarimetric measurements. This was fatal to the study of rotatory dispersion, since no other monochromatic light could be produced with equal ease. Organic chemists became accustomed to determine the rotatory power of the ever increasing number of optically active compounds for the sodium doublet only; this was pardonable in their case for lack of experimental technique. There was, however, no justification for the physical chemists, seeking to discover the influence of solvent, concentration, temperature, or chemical constitution on rotatory power to work with sodium light only and to record a single point on the curve of rotatory dispersion of unknown form. This work has met with little success, as the effects produced by variation of temperature, or by dilution with different solvents so complex that no simple rules have been discovered. The influence of the wave-length of the light is, however, simpler and should be studied for two reasons. In the first place, it is of no use to seek to establish fundamental laws with the help of measurements which are restricted to only one wave-length. The form of the dispersion curve should be determined. Secondly, the effect of change of wave-length on rotatory power is not accompanied by any change in the medium, whereas changes of temperature, solvent and concentration may introduce complications by altering the structure of the molecule. These considerations demand the study of dispersion as a preliminary to all investigations on optical activity, with a view to determine the type to which the dispersion curve of the material under examination belongs.

The study of rotatory dispersion has been of great value in another direction also. It has provided us with a new method for distinguishing isomeric, tautomeric and polymeric from polymorphic optically active substances.<sup>23</sup>

### *Experimental Methods of Measuring Rotatory Dispersion in the Different Regions of the Spectrum.*

*Rotatory Dispersion in the Visible Region.*—The experimental determination of rotatory dispersion in the visible region has been rendered easy by the introduction of new sources of light, such as the enclosed mercury and cadmium<sup>24</sup> arc-lamps as well as the

cadmium-silver arc burning between a vertical and a horizontal electrode. Additional lines of sodium and lithium are rendered available by suitably introducing salts of these metals into the carbon arc. The spectra of these metals are so simple that no elaborate purification is required. A direct vision prism on the eye-piece as employed by Perkin<sup>25</sup> is sufficient to read these lines and avoid the presence of stray light. A wide slit opening symmetrically in front of the triple-field is the only other modification which has to be made in adapting an ordinary polarimeter for measurements of rotatory dispersion. The routine measurements are carried out for about 10 wave-lengths distributed along the visible spectrum as follows :

Li	Cd	Li	Na	Hg	Hg	Ag	Cd	Cd	Hg
6708	6438	6104	5893	5781 (mean)	5461	5209	5086	4800	4358
Red		Orange		Yellow		Green		Blue	Violet

If additional lines are required, they can be easily obtained from the line spectra of copper, zinc (in the form of brass) and silver. But on account of the greater complexity of these spectra, it is necessary to narrow down the triple-field of the polarimeter by means of the slit in order to prevent overlapping, and to illuminate the polarimeter by light which has already passed through a spectroscope before being thrown into the triple-field. These additional lines are as follows :<sup>26</sup>

Zn	Cu	Cu	Ag	Ag	Cu	Cu	Cu	Zn	Zn	Zn
6862	5782	5700	5472	5465	5218	5153	5106	4910	4732	4680
Red	Yellow		Green				Blue			

*Rotatory Dispersion in the Ultraviolet Region.*—The study of the rotatory dispersion in the ultraviolet region has assumed great importance, as it is especially in this region that the essential characters of the dispersion curves are first disclosed. Several photographic methods have been used at different times. The method of Joubin<sup>27</sup> is now only of historical interest. The method of Nutting<sup>28</sup> was a notable advance in the technique of rotatory dispersion work. From the measurements of the displacement of fringes for each spectral ray, the rotatory power is calculated. The relative error in this method is, however, very

great. In the other methods which have been used, the complete extinction of a single field is replaced by that of two or three contiguous fields of different intensities. On one side of the extinction, one of the fields is very dark, while the other is bright; reverse is the case on the other side; whilst between these two extreme positions there is equality of intensity of the different fields which corresponds to complete extinction. It is indicated by an abrupt change in the intensity of illumination of the different portions of the field. These methods arranged chronologically are those of St. Landau,<sup>29</sup> Lowry,<sup>30</sup> Darmois,<sup>31</sup> and Kuhn.<sup>32</sup> The method of Lowry is very precise and allows any accidental displacement of the apparatus to be disclosed by the inequality of illumination of the exterior fields. In this method an iron-arc is used as a source of illumination, and the telescope of the analyser is replaced by a long-focus lens, by means of which a real image of the triple field is thrown on to the slit of the spectrograph. The spectrum which is formed in the spectrograph is divided into three horizontal strips corresponding to the three portions of the triple field, and measurements of the rotatory power are made by observing the wave-length at which the three divisions of the spectrum lines are equally bright for a given setting of the analyser. For lower down the ultraviolet region, the Nicol prisms are replaced by Foucault prisms and for still lower wave lengths, all the calcite must be eliminated from the apparatus, *e.g.*, by replacing the Foucault by Rochon prisms, and the quartz-calcite lenses by quartz or quartz-fluorite.

The instruments of Landau, Darmois and Lowry require trial and error to find out the rotations through an extended spectral interval, especially when multiple line-spectra are used. This is eliminated in the apparatus of Cotton and Descamps.<sup>33</sup> Their instrument is based on the principle that the rotatory movement of the analyser produces a displacement of the image recorded on the sensitised plate. Light which has passed through the polariser, and a trough containing the liquid and the analyser, along an axis  $xx'$  is deflected at right angles to this axis by a train of prisms. It falls on a photographic film bent into a cylindrical form with  $xx'$  as the axis of the cylinder, forming upon it a series of images of a short slit for the different ultraviolet lines of the mercury arc-lamp employed for illumination. The analyser and the train of prisms are mounted together, so that they form a system which can be rotated

about the  $x\ x$  axis. The light spots move over the photographic plate, which registers their intensities for different positions of the analyser, making it possible to determine the angle at which each of them is extinguished. In the instrument as constructed, the first prism of the train also acts as the analyser, being made of Iceland spar; the second prism is of quartz, and the necessary lenses and the trough walls are transparent to ultraviolet rays. The rotatory dispersion is determined by giving two exposures, the first in the absence of the active substance, and the second with the latter in the apparatus. The first film records the extinctions which are produced for all the lines simultaneously (polarimetric zero); the second film gives the extinctions for the active substance. The exact positions of the extinctions on the negatives are deduced from a study of the photographic density of the images by means of the reading microphotometer of Challenge and Lambert.<sup>34</sup>

#### *Rotatory Dispersion in the Infra-red Region of the Spectrum.*

The infra-red measurements are made with a triplefield polarimeter having Nicol prisms of large aperture.<sup>35</sup> The light from a Nernst lamp is focussed through this apparatus on the slit of the infra-red spectrometer, having a sensitive thermopile fitted in the focus of the eye-piece of the telescope. The intensity of the transmitted radiations is measured by means of the galvanometer deflections for different settings of the drum of the spectrometer. Work in the infra-red region is difficult not only on account of the increasing weakness of the radiation, but also on account of the extremely low rotatory power,

#### *Types of Rotatory Dispersion.*

Although Biot had discovered the law of inverse squares in 1817, and the errors in the law in 1836 as already remarked, the experimental data on rotatory dispersion at his disposal were not sufficiently accurate to enable him to correct the law,  $\alpha = k/\lambda^2$ . His graphical method of plotting  $1/\alpha$  against  $\lambda^2$ , which he had employed in testing the law, would have shown that the straight line does not pass through the origin at  $\lambda^2 = 0$ , but intersects the axis of zero rotation at a finite distance from the origin, i. e., at a point given by  $\lambda_0^2 = \lambda_0^2$ . The true law of rotatory dispersion then becomes  $\alpha = k/(\lambda^2 - \lambda_0^2)$ , instead of  $\alpha = k/\lambda^2$ . In 1898, Drude<sup>36</sup> as the result of a long



theoretical investigation, based on the electronic theory of radiation, first enunciated the law of rotatory dispersion in the general form

$$\alpha = \frac{k}{\lambda^2} \sum \frac{\theta_h f_h N_h}{1 - \frac{\tau_h}{T}} = \frac{k_n}{\lambda^2 - \lambda_n^2} \text{ (approximately),}$$

where the "dispersion constants"  $\lambda_n^2$ , corresponding with the natural free periods  $1/\lambda_n$  of the electrons, were deduced from measurements of the refractive dispersion, according to the equation,

$$N^2 = E + \sum \frac{M_n}{\lambda^2 - \lambda_n^2}$$

in which  $N$  is the refractive index, and  $E$  is the dielectric constant of the medium. The generalised formula of rotatory dispersion did not find any application for many years, except in the solitary case of quartz by Drude himself as a two-term equation. The reason for this is not far to seek. Although a vast number of optically active substances were prepared and studied, the rotatory power of a great majority of them had been determined for one wavelength only. Lowry<sup>37</sup> for the first time in 1913 showed that the single term of Drude's equation, involving only two arbitrary constants, namely, a "rotation constant" and a "dispersion constant"  $\lambda_0^2$ , as set out in the equation  $\alpha = k/(\lambda^2 - \lambda_0^2)$ , was sufficient to express the rotatory dispersion of a large number of secondary alcohols of the aliphatic series. Further applications of Drude's simple formula were made by him<sup>38</sup> with about 37 compounds of the terpene series for which Rupe<sup>39</sup> had published in 1915 a series of measurements of the rotatory power for four different wavelengths.

### *Simple and Complex Dispersion.*

As a result of this work, Lowry<sup>40</sup> has classified rotatory dispersions as "simple" or "complex," according as they can or cannot be expressed by the equation,  $\alpha = k/(\lambda^2 - \lambda_0^2)$ . This equation which differs from Biot's equation only by the addition of the constant  $\lambda_0^2$  was deduced by Drude for rotatory dispersion in transparent media; it does not, therefore, apply to the absorbent media studied by Cotton<sup>41</sup> where anomalies are observed on passing through the region of absorption.

*Examples of Simple Dispersion.*

This simple formula is valid for a large number of secondary alcohols<sup>37</sup> and for nicotine<sup>42</sup> containing a single asymmetric carbon atom. It is also valid for methylcyclohexylideneacetic acid<sup>43</sup> which contains no asymmetric carbon atom. Other substances which obey the simple dispersion law are camphorquinones, oxymethylenecamphors<sup>45</sup> and their condensation products with aromatic amino compounds,<sup>46</sup> the rotatory dispersion of which has been investigated by the present writer. An inspection of the structural formulae of these compounds, which contain two, four or six asymmetric carbon atoms, reveals the fact that they are complex ring compounds loaded with double bonds. Sucrose<sup>46a</sup> containing nine asymmetric carbon atoms, also shows simple rotatory dispersion. It is evident from these examples that the type of rotatory dispersion which a substance exhibits depends neither on its molecular structure, nor on the number of asymmetric centres which it may contain. These researches on the optical rotatory dispersion of organic compounds carry us back to the classical postulate of Molecular Dissymmetry of Pasteur, who attributed rotatory power to the dissymmetry of the whole molecule rather than to the presence of one or more asymmetric carbon atoms in it.

*Examples of Complex Dispersion.*

The rotatory dispersion of camphor and of most of its derivatives cannot be expressed by the equation,  $\alpha = k/(\lambda^2 - \lambda_0^2)$ ; it is therefore, not simple but complex. In nearly every case, however, it can be expressed by using two terms of Drude's equation,<sup>47</sup> although the dispersions are normal as in the case of camphor itself (where the rotations are positive) and sometimes anomalous as in the case of  $\alpha'$ -bromocamphor, the dispersion curve of which shows all the three characteristic anomalies, namely, an inflexion at 5455 Å.U., a maximum at 4710 Å.U. and a reversal of sign at 3890 Å.U. Another example of anomalous rotatory dispersion, observed by the present writer, is the monoacetyl derivative of *p*-phenylenebis-aminocamphor<sup>48</sup>. The rotatory dispersion curve of this substance in pyridine solution cuts the axis of zero rotation between the mercury green and violet regions of the spectrum, and thus exhibits one of the three characteristic anomalies, namely, reversal of sign.

*Anomalous Rotatory Dispersion.*

The small correction which is needed to convert Biot's law into the Law of Simple Rotatory Dispersion is of great importance, since if all optically active substances obeyed the Law of Inverse Squares, all rotatory dispersions would be normal and would be identical *e.g.*,

$$\alpha_{4358}/\alpha_{5464} = \frac{(5464)^2}{(4358)^2} = 1.52$$

In this case no form of anomalous rotatory dispersion could exist. The introduction of a second term into the equation of the rotatory dispersion gives rise to complex rotatory dispersion, and the two-term formula may be written thus

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_2}{\lambda^2 - \lambda_2^2}$$

The examination of this equation discloses the fact that  $\alpha$  is a maximum at the wave-length  $\lambda$ , *i.e.*, anomalous dispersion can occur, if

$$\frac{k_1}{k_2} = \frac{(\lambda^2 - \lambda_1^2)^2}{(\lambda^2 - \lambda_2^2)^2}$$

a condition which can be fulfilled when  $k_1$  and  $k_2$  are of opposite sign, and  $k_2 > k_1$ , when  $\lambda_1 > \lambda_2$ . From the chemical point of view, this anomaly expressed by the two-term formula is due to the presence in the liquid of two kinds of optically active molecules, possessing normal rotations of opposite sign and of unequal dispersion. This suggestion is due to Biot<sup>48</sup> who in 1836 produced this anomaly artificially by two methods when he attempted to compensate the optical rotatory power of *laevo*-rotatory turpentine by balancing it against a column of *dextro*-rotatory oil of lemon, in which the superposition is entirely optical, or by mixing the two liquids in suitable proportions.

The anomalous rotatory dispersion of tartaric acid was explained by Arndt<sup>49</sup> in 1858 as due to the presence of two interconvertible forms of the acid, which, however, have never been isolated. It is for this reason, that special interest attaches to the work of Austin

and Park<sup>50</sup> on the rotatory dispersion of *laevo*-rotatory diacetyl tartaric acid, and its *dextro*-rotatory anhydride. Both these compounds exhibit simple dispersion in dry acetone (the *dextro*-rotatory compound having smaller dispersion constant), which may be expressed by the equations :

$$\left[ \alpha \right]_{\lambda}^{20^{\circ}} = -6\,508 / (\lambda^2 - 0\cdot0838)^2 \text{ (acid),}$$

$$\left[ \alpha \right]_{\lambda}^{30^{\circ}} = +18\,354 / (\lambda^2 - 0\cdot0507)^2 \text{ (anhydride).}$$

In wet acetone, the anhydride undergoes gradual hydrolysis into the corresponding acid. Since the rotations of the two compounds are opposite in sign, and their dispersion constants are of unequal magnitude, all the conditions necessary to produce anomalous dispersion are present in the solution of a mixture of the two compounds. Thus a freshly prepared solution of the anhydride in wet acetone which gave a *simple dextro-rotation* soon showed a *complex and anomalous* dispersion, owing to the development in the free acid of a negative partial rotation with a high dispersion coefficient. This *complex and anomalous* dispersion was transformed in turn into a *complex and normal* dispersion when the negative term had become predominant over the whole range of wave-lengths; and finally the solution, after complete hydrolysis shows only the *simple laevo-rotation* of the free acid.

The rotatory dispersion of certain coloured substances is always anomalous in the immediate neighbourhood of an active absorption band, namely, the absorption band which is really caused by the same radicals in the molecule that are responsible for its optical activity. In the neighbourhood of such an absorption band, Drude's simple formula does not apply owing to the fact that in deducing it, certain terms, the effect of which is appreciable only in the neighbourhood of an absorption band, are neglected. If these terms are retained, then theory leads to the result that in the neighbourhood of an absorption band, the dispersion curve after passing through a maximum, changes sign, and then passes through a second maximum of the opposite sign. The theory further requires that between the two maxima, the phenomenon of *circular dichroism* (the unequal absorption of two circularly polarised rays into which the original plane vibration can be resolved) should be observable. The double maxima and the circular dichroism at an absorption band were first

observed by Cotton<sup>51</sup> in 1896 and the phenomenon is known as the "Cotton Effect."

The applications of the study of circular dichroism to the solution of one of the most fundamental problems in natural science namely, the realisation of a *complete asymmetric photosynthesis* affords yet another instance in which the Science of Optics has rendered great service towards the elucidation of the great riddle which has puzzled the scientists since the time of Pasteur. Starting with optically inactive materials, the synthetic products of the laboratory are always racemic compounds or externally compensated mixtures of the oppositely active antipodes. These products never show any optical activity until and unless they have been resolved by one of Pasteur's methods. The products synthesised by the living plant or animal from inactive materials, such as water, carbon dioxide, ammonia, etc., are generally endowed with optical activity, and thus present a striking contrast in this respect. The direct production of optically active substances, therefore, seemed to be the very prerogative of life. Pasteur himself was led in 1860 to believe in the deep and unbridgeable gulf between the chemistry of the living and that of dead matter. Although he modified this opinion<sup>52</sup> in 1884, the vitalistic views of Japp and others<sup>53</sup> expressed as late as 1898 show the existence of the belief in the great barrier between the products of the laboratory and those of life. The products of natural synthesis by plants or animals always show the same optical activity. It is the result of a partially asymmetric synthesis brought about by the presence of pre-existing optically active molecules in the living cell. The realisation of a *partially asymmetric synthesis* by Marckwald and Mackenzie<sup>54</sup> in 1900 for the first time in the laboratory has thus brought the natural synthesis by plant or animal within the scope of chemical mechanics, having reduced it to be simply a question of relative difference in reaction velocities. These researches, however, still leave unanswered the question of the origin of the first optically active substance, the presence of which has served to guide and influence the natural syntheses, taking place in plant and animal cells during all the subsequent periods. The realisation of a complete asymmetric synthesis, from substances devoid of any optical activity, will be therefore a great experimental triumph. Several attempts made with the aid of photochemically sensitive asymmetric substances, showing circular dichroism, such as those by Henle and Haack<sup>55</sup> in 1908, Cotton<sup>56</sup> in 1909 and

Jaeger<sup>57</sup> in 1921 proved, however, unsuccessful. Recently Kuhn and Braun<sup>58</sup> working with Freudenberg announced that they have obtained a positive result by making use of the procedure which had been previously indicated by Cotton. They found that the rotatory power of ethyl  $\alpha$ -bromopropionate,  $\text{CH}_3 \cdot \text{CH} \cdot \text{Br} \cdot \text{COOEt}$ , in alcoholic solution first increases enormously, then decreases and finally changes sign as the wave-length is decreased. From these measurements of rotatory dispersion, they inferred that the substance exhibited circular dichroism. They, therefore, exposed ethereal solutions of the corresponding racemic ester simultaneously to *dextro*- and *laevo*-circularly polarised light of  $\lambda = 2800 \text{ \AA}$ . The maximum rotation observed in ether was only  $\pm 0.05^\circ$ . Further progress in the preparation of optically active substances by the help of circularly polarised light has been recorded by Kuhn.<sup>59</sup> It is found that when 1.5 per cent hexane solutions of racemic dimethylamide of  $\alpha$ -azidopropionic acid,  $\text{CH}_3 \cdot \text{CH} \cdot \text{N}_3 \cdot \text{CO} \cdot \text{N} (\text{CH}_3)_2$ , were partly decomposed by circularly polarised light ( $\lambda = 3100 \text{ \AA}$ ), and the undecomposed dimethylamide subsequently isolated from the solution, active preparations which showed rotation of  $+0.78^\circ$  and  $-1.04^\circ$  were obtained. The problem is thus solved in principle, and for more complete separation two conditions should be satisfied. The first is that the racemic substance should be completely dissociated in solution, and secondly we should know the spectral region in which the circular dichroism is maximum, so as to enable us to select the radiation which would give the maximum separation. The method has the advantage that it allows the production of both the isomers.

Apart from the application of circular dichroism to the preparation of the optically active substances from purely inactive materials and without the intervention of any vital processes or agencies, its utility in the solution of other physico-chemical problems is also being recognised. The existence of circular dichroism enables us to establish a very sharp distinction between the solution of a racemate and that of a simple mixture which is inactive by external compensation<sup>60</sup>. A study of circular dichroism also allows us to throw light on the nature of the chemical bond. Whenever a liquid shows circular dichroism, it is certain that it contains molecules which are active and at the same time absorbent. Lifschitz<sup>60</sup> from a study of some complex derivatives of cobalt has been able to recognise in them two components one active (*i.e.*, containing an asymmetric

carbon atom) and the other absorbent (i.e., a coloured ion). He distinguishes between the case in which the two components are linked by a principal valency bond, and that in which they are united by an electro-valent bond. It is only in the former case that circular dichroism would be manifest; in the other case, in which the linking between the components is electrovalent, no influence of absorption on the optical activity of the dissolved substance would be observed.

The application of other branches of Optics, such as X-ray methods, has yielded important results, and has led to definite advances in our knowledge of crystal structure, but enough has been said to show the immense debt which chemistry owes to the Science of Optics

In concluding this address. I would like to make some suggestions which may prove useful to our young chemists during the period of their university studies. Most of the easy problems in Chemistry have been solved, and what remains to be accomplished is difficult. It is, therefore, necessary that the future investigators in chemistry should be properly trained in the fundamental Sciences, namely, Mathematics and Physics. If their work is to lie in Bio-chemistry, they should pay special attention to Biology and Physiology. Above all, skill in experimental technique is of the utmost value. As most of the original work in Chemistry is published in English, French and German, a good working knowledge of these languages should be the first preliminary preparation for all such studies. If the Indian chemists are thus equipped, we may certainly hope to see as great advances made in Chemistry in this country as have already been accomplished in Physics. The Indian mind, on account of its great development during the long period of civilisation it has witnessed, is eminently fitted for scientific investigation. What is needed is proper equipment of the workers with the necessary tools for the task before them, and when this is done, fundamental discoveries are sure to follow.

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# Variation of the Electrical Charge of Colloidal Particles

## Part V. Effect of the Manner of Preparation of Arsenious Sulphide Sol on the Cataphoretic Speed in Presence of Electrolytes.

By JNANENDRANATH MUKHERJEE, SATYAPRASAD ROYCHOU DHURY  
AND SOURESWAR GOHAIN RAJKUMAR.

The manner of variation of the cataphoretic speed of particles of this sol with different concentrations of the same electrolyte depends on the method of preparation or the dilution (Mukherjee and Choudhury, *J. Indian Chem. Soc.*, 1925, 2, 296 ; Mukherjee, Roychoudhury and Bhattacharyya, *ibid.*, 1928, 5, 735). Two different types of curves have been met with; in one the cataphoretic speed continually decreases with the concentration of the electrolyte (Mukherjee and Choudhury, *loc. cit.* ; Mukherjee, Choudhury and Roychoudhury, *ibid.*, 1927, 4, 493 ; Freundlich and Zeh, *Z. phys. Chem.*, 1925, 114, 84) and in the other there is a fall in the cataphoretic speed at low concentrations of the electrolyte but an increase at higher concentrations (Mukherjee, Roychoudhury and Bhattacharyya, *loc. cit.* also Kruyt and Willigen, *Z. physikal. Chem.*, 1927, 130, 17). It has also been observed that on dilution, a sol with a lower initial charge shows a rapid increase in the charge at lower concentrations of potassium chloride. These observations are of interest in relation to the properties of the primarily adsorbed ions including their valencies and the adsorption of the ions present in the solution (Mukherjee, *Trans. Faraday Soc.*, 1921, 16, 103). The concentration of hydrogen sulphide, of hydrogen ions and of arsenious oxide are expected to have an important effect on the relative amounts of sulphide and hydrosulphide ions on the surface. S. N. Mukherjee (*Kolloid Z.*, 1930, 53, 159) has shown that on the addition of arsenious oxide the cataphoretic speed of arsenious sulphide sol diminishes. One can visualise the possibility that when added in very small quantities it may increase the charge as the hydrogen ion concentration would be lowered and a larger proportion of sulphidions is present. This would happen when the amount of free sulphidions and hydrosulphidions adsorbed on the

surface is not sufficiently decreased owing to the diminished equilibrium concentration of hydrogen sulphide in the solution which is a necessary consequence of the addition of arsenious oxide. This expected rise has been observed using an amount of arsenious oxide (equivalent to a concentration of 0.0001N) lower than that used by S. N. Mukherjee (*loc. cit.*).

In the light of the theoretical consideration advanced in previous papers (*loc. cit.*) a difference in the relative adsorbabilities of the cation and anion should produce a difference in the slopes of the curves (see in particular Mukherjee, Roychoudhury and Bhattacharyya, *loc. cit.*). The electrical adsorption of two univalent cations by a primarily adsorbed divalent anion is of interest as showing the effect of the diameter of the ions.

#### EXPERIMENTAL.

The sol prepared as previously described was kept wrapped with black paper in a dark place.

The salts used were all of Merck's reagent quality twice recrystallised. The temperature of the thermostat was  $35^{\circ} + 0.1^{\circ}$ .

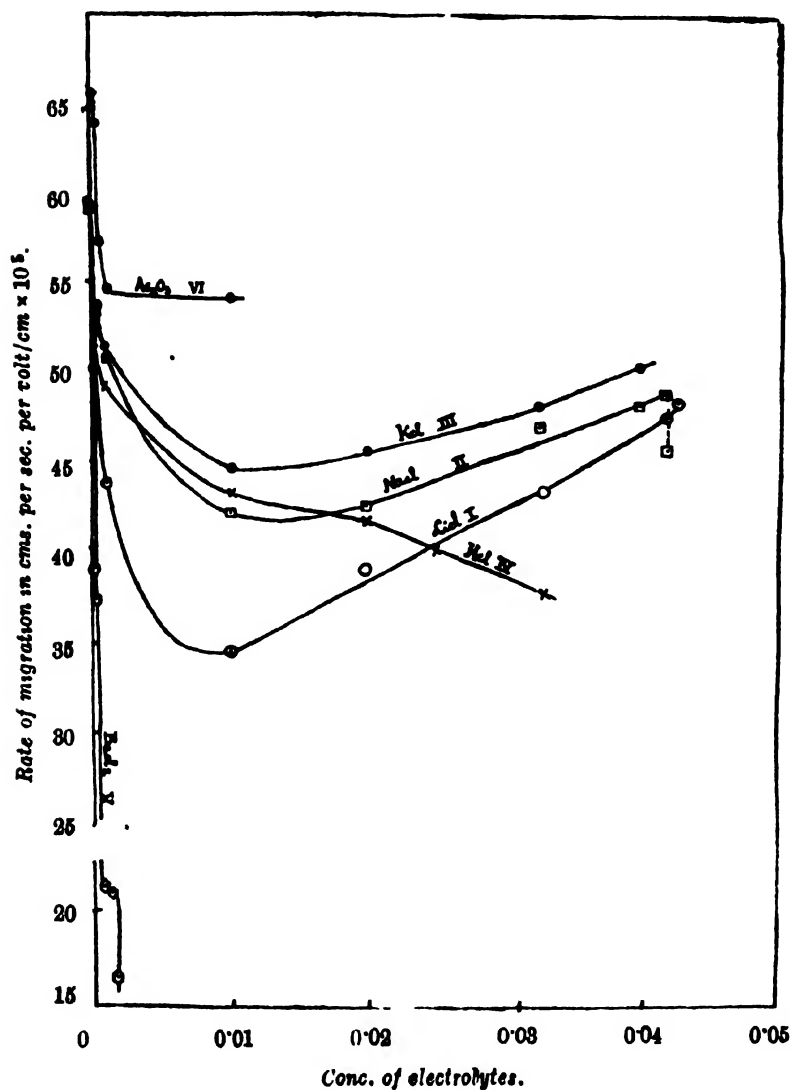
Corrections for viscosity were neglected as they were within the limits of the error. In view of the errors possible at low concentrations some of the data are given below to show the accuracy and to show how far the observed speed is independent of the direction of motion (Mukherjee, *Kolloid Z.*, 1932, 58, 155).

TABLE I.

*Rate of migration in cms. per sec. per volt/cm  $\times 10^5$ .*

Electrolyte conc.	Direct.	Reverse.	Mean.
0	58.33 } 60.56 }	59.48 } 58.91 }	59.84
LiCl 0.0002 N	53.95 } 54.61 }	54.29 } 52.78 }	53.92
NaCl 0.0002	53.12	53.94	53.5
KCl 0.0002	53.62	52.10	52.86
HCl 0.0002	52.14	50.84	51.5
BaCl <sub>2</sub> 0.0001	40.00	38.89	39.19
As <sub>2</sub> O <sub>3</sub> 0.0001	67.74	64.12	65.9

The cataphoretic speeds are shown in the Figure. Duplicate experiments were performed in most cases.



### DISCUSSION.

#### *The Influence of Arsenious Oxide.*

1. While the diminution of the cataphoretic speed on addition of arsenious oxide is in keeping with its sensitising effect at all concentrations so far investigated (S. N. Mukherjee, *loc. cit.*) against coagulation by electrolytes, the increase observed here shows that higher

cataphoretic speed does not always confer a greater stability against coagulation by electrolytes. Reference may be made in this connection to the greater rate of diminution of the positive charge of a ferric oxide sol on the addition of potassium chloride when the initial cataphoretic speed is higher (Mukherjee, Roychoudhury and Biswas, *J. Indian Chem.Soc.*, 1931, 8, 373).

2. On account of the strong affinity of sulphidions for hydrogen ions only a small proportion of the total free negative charge of the surface is present in the form of primarily adsorbed sulphidion. On the addition of arsenious oxide the equilibrium concentration of hydrogen sulphide as also the amount of it that is adsorbed on the surface decreases. It is possible, however, that at one stage though there is a smaller total number of sulphide and hydrogen sulphide ions on the surface, the density of the charge will be greater on account of a greater proportion of sulphidions which carry two units of charge. The observed rise indicates that the limits within which this rise takes place are very small.

#### *The Influence of Alkali Chlorides.*

1. A comparison of the curves in the figure with those previously observed with this sol (*loc. cit.*) show that both hydrochloric acid and barium chloride uniformly decrease the cataphoretic speed. But the rate of decrease in the present case is definitely greater. The existence of a greater proportion of divalent sulphide ions will increase the electric adsorption and the greater slope of these curves is in agreement with the theory. But the uniformly lower value of the cataphoretic speeds which shows that the capacity of the three alkali chlorides to diminish the negative charge is in the order  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$  is contrary to previous observations as also the order of coagulating concentrations of these electrolytes. A difference is also noticed in the slopes of the ascending and descending portions of the curves. If the greater slope of the portions of the curves where the cataphoretic speed steadily diminishes be referred to the adsorption of cations then the adsorbability of these three cations appears to be in order  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ . On the other hand after reaching the minimum which, it may be noted, is reached at about the same chlorine ion concentration, the cataphoretic speed increases more rapidly in the case of lithium and the positive (increasing cataphoretic speed) slopes are also in the order  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ .

The assumed stronger adsorption of lithium ions cannot account for this order. If the increase in the negative charge be attributed to the adsorption of chlorine ions, then two explanations of this difference in the positive slope are possible: either (i) that the lower negative charge facilitates a stronger adsorption of the anion (chloridion) or (ii) that the adsorption of the cations is in the order  $K^+ > Na^+ > Li^+$ . The former explanation is in conformity with the observation that a lower initial cataphoretic speed favours a rise in the negative charge as shown by an increased cataphoretic speed on the addition of potassium chloride. If this explanation is true it is not necessary to assume that there is a reversal in the order of adsorption of the cations in the ascending portion of the curves. There is, however, one fact which seems to contradict the order of adsorption:  $Li^+ > Na^+ > K^+$ . This is that at 0.0002N the cataphoretic speeds indicate the order of adsorption  $K^+ > Na^+ > Li^+$  as shown by the following respective values of the speeds: 52.86, 53.52, 53.92.

2. On theoretical grounds it is difficult to understand why the relative orders of adsorption of the cations will be different in different portions of the curves. Assuming that the order of adsorption of the cation is  $Li^+ > Na^+ > K^+$  two difficulties are met with: of this, one has been referred to just now and consists in the cataphoretic speeds at 0.0002N salt concentration and the other is the slope of ascending portion which is uniformly greater for lithium and decreases in the order  $Li^+ > Na^+ > K^+$  up to the coagulating concentration. If the lower negative charges were the cause of the difference in the slopes, as suggested in the previous paragraph then the slope should decrease as the negative charge increases. The curves do not support this conclusion. The other possible explanation is that the order of adsorption of the cation is really  $K^+ > Na^+ > Li^+$  as observed with this sol prepared in a different way. The apparently opposite order of adsorbability is to be attributed to the fact that there is a large proportion of divalent sulphidion on the surface and that the simultaneous electrical adsorption of two univalent cations by a divalent anion depends also on the repulsion between the univalent cations. The ions are assumed to be electrically adsorbed in a hydrated condition and the diameters of the hydrated ions are assumed to be in the order,  $Li^+ > Na^+ > K^+$  which conforms with the mobilities. The simultaneous electrical adsorption of two lithium ions will be easier but that of two potassium ions more difficult on account of

the smaller diameters of the potassium ions. With the result that at the smallest concentration where only one cation is adsorbed by a divalent ion, the order of cation adsorption should be  $K^+ > Na^+ > Li^+$  as is shown to be the case at 0.0002N. When the adsorption of two cations become more and more in operation there is a change in the apparent adsorption order  $Li^+ > Na^+ > K^+$ . This persists till the greater adsorption of the chlorine ions asserts itself at the higher chlorine ion concentration at about 0.01N. The surface is now mostly covered by univalent anion 'complexes' and the usual order  $K^+ > Na^+ > Li^+$  is reflected in the positive (increasing negative charge) slopes which is greater for the more weakly adsorbed cation. This explanation also enables us to understand the regular diminution of the speed observed in other sols and the usual order of cation effect on the speed, *viz.*,  $K^+ > Na^+ > Li^+$ . In the usual method of preparation, the sol is saturated with hydrogen sulphide which is driven with a current of hydrogen whereas in the other group of sols excess of arsenious oxide is ensured. The two groups of sols probably differ in that in the former the anions are mostly univalent and that in the second there is a considerable proportion of divalent anions.

3. The order  $Li^+ > Na^+ > K^+$  is known and the adsorption of these ions in a dehydrated condition would explain such an order from the point of view of the electrical adsorption. Only further experiments can decide between these alternatives.

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# An Automatic Glass Burette Jet.

By D. R. PARANJPE AND D. V. CHANDERKAR.

The burettes used in Intermediate Chemistry laboratories are usually cheap ones without ground glass stoppered jets. In ordinary practice they are provided with a separate jet connected with the drawn out end of the burette and the flow is controlled by a pinch-cock. These pinch-cocks are easily spoilt and cause a permanent stricture in the connecting rubber tube.

The automatic jet, described here, does away with the pinch-cock. It may be used also on the delivery tubes of Kipp's  $H_2S$  generators, thus stopping much wastage of the material when the generator cock is inadvertently left open. The jet is extremely simple to make and has replaced the pinch-cock in this laboratory.

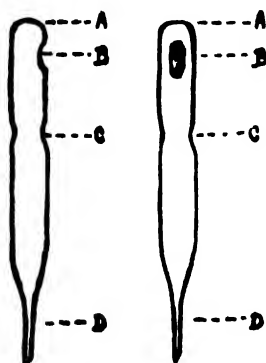


FIG. 1. FIG. 2.

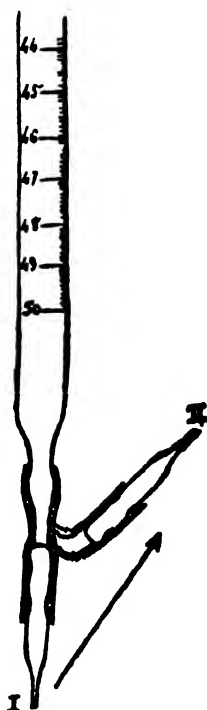


FIG. 3.

To make an automatic jet, an ordinary jet is first drawn as at D (Figs. 1 and 2). The tube is then closed at A and a small circular

opening made at B as shown. A slight drawing out of the tube as shown at C will be found useful.

To work the jet, a tight fitting rubber tube is slipped on up to the constriction C, where it can be tied on with a piece of thread, so as to cover the circular hole B.

No liquid will flow out when the burette is filled and the circular hole on the jet covered with rubber tubing as shown in Fig 8. To release the liquid, the rubber tubing is pinched at a spot immediately above the circular hole B (Fig. 2). When the rubber tube is lifted up in this way, the liquid from the burette enters the hole B and escapes through the jet. The flow can be easily controlled by pressing on the rubber tube connection, and with little practice even control over drops can be attained.

While using the jet it is very important that it should be freed from air-bubbles, otherwise titration errors will occur. To get rid of the air bubbles the flow is to be started as explained above and the jet turned from position (I) to position (II) as shown in Fig. 3.

If alkalis are used in the burette, there is danger of the rubber connection becoming slippery and so moving its position, thus causing a wrong reading. This is corrected by tying a piece of thread on the part D (Fig. 1) and fixing it there permanently.

## On the Stability of Lithium Urate Sols.

BY SATYA PRAKASH.

It was observed by Schade and Boden (*Z. physiol. Chem.*, 1918 88, 847) that if uric acid be suspended in boiling water, and then lithium hydroxide added to it, the acid gradually passes into the solution. On addition of sodium chloride to the colloidal lithium urate so formed, the unstable jellies of the substance are obtained. In this communication, an investigation of the substance has been made from the view point of its stability as given by coagulation and conductivity results.

The sols of lithium urate were prepared by suspending 2 g. of uric acid in 100 c.c. of conductivity water, to which a drop of phenolphthalein was added. The solution was warmed to 80-90° when lithium carbonate in very small quantities was added, till a faint pink colour just appeared. Lithium carbonate was given preference over the hydroxide on account of its insolubility. Thus a clear solution of lithium urate was obtained. It was allowed to cool slowly to the room temperature, and then filtered. The sol thus obtained is very unstable and precipitates out in the course of 20 hours. In the following table, the results on the coagulation of the sol by different electrolytes have been given.

TABLE I.

Amount of the sol taken = 2 c. c. Time of observation = 30 mins.

Total volume = 4 c. c.

Electrolyte.	Amt. required to coagulate.	Coagulating conc. in normality.
N-KCl	0.3 c. c.	0.075
N- $\text{K}_2\text{SO}_4$	0.4	0.1
N/500-BaCl <sub>2</sub>	0.4	0.0002
N/110.6-Al (NO <sub>3</sub> ) <sub>3</sub>	0.9	0.00025
N/66.5-H <sub>2</sub> SO <sub>4</sub>	1.4	0.00526
N/50.Oxalic acid	0.8	0.004

Lithium urate forms a negatively charged sol. The coagulation power of the electrolytes is in the following decreasing order:  $\text{BaCl}_2 > \text{Al}(\text{NO}_3)_3 > \text{H}_2\text{C}_2\text{O}_4 > \text{H}_2\text{SO}_4 > \text{KCl} > \text{K}_2\text{SO}_4$ .

The apparent anomaly of barium chloride from the well known Schulze-Hardy law is due to the chemical action between the barium salt and lithium urate.

The effect of dilution on the stability of the sol is given in the following table.

TABLE II.

Total volume = 4 c. c. Time of observation = 30 mins.

Electrolyte.	Amt. of electrolyte in c. c. to coagulate		
	1 c. c. sol.	2 c. c. sol.	2.5 c. c. sol.
N-KCl	1.0	0.8	0.15
N- $\text{K}_2\text{SO}_4$	0.8	0.4	0.25
N/500- $\text{BaCl}_2$	0.8	0.4	0.25
N/110.8 $\text{Al}(\text{NO}_3)_3$	0.6	0.9	1.1
N/66.5- $\text{H}_2\text{SO}_4$	1.0	1.4	1.5
N/50-Oxalic acid	0.6	0.8	0.9

The results recorded in this table show that lithium urate becomes stable on dilution when coagulated by electrolytes like potassium chloride or sulphate and barium chloride. However, when the coagulation is effected by aluminium nitrate or oxalic and sulphuric acids, the concentrated sol takes up more electrolyte than the diluted sol. Ghosh and Dhar (*J. Phys. Chem.*, 1927, 31, 187) have shown that the sols of antimony sulphide, prussian blue, gum dammar, and gamboge do not follow the general dilution rule and hence behave abnormally when coagulated by univalent and sometimes bivalent ions. Lithium urate also appears to belong to this abnormal class. The author has observed that while a sol obtained by suspending 2 g. of uric acid in 100 c. c. is only stable for 20 hours, the sols obtained by suspending 0.5 g. or less of uric acid in the same volume can be preserved for a number of days. It appears that on dilution, the sol preferentially adsorbs the similarly charged ions to a large extent, and it has also a marked tendency of adsorbing chloride or sulphate ions from the salts when the coagulation is affected by them. On dilution, the sol undergoes marked hydrolysis, and the uric acid thus formed is further stabilised by the adsorption of hydroxyl ions from lithium hydroxide, a product of hydrolysis.

When the sol is coagulated by potassium chloride in presence of phenolphthalein, the pink colour is intensified, showing the liberation of hydroxyl ions. The same behaviour is observed when the sol is precipitated under the ageing influence alone (*cf.* Young and Musgrave, *Biochem. J.*, 1932, 26, 941). It has been observed that a sol having a  $p_H$  7.6 became so much alkaline as to give a  $p_H$  8.6 after 3 days. In the following table, the influence of ageing on the hydrogen ion concentrations of three sols prepared by the use of different amounts of lithium carbonate has been recorded.

TABLE III.

1 G. of uric acid suspended in 50 c. c. of water.

$Li_2CO_3$ used.	Initial $p_H$ .	$p_H$ after 3 days.
0.2 g.	7.5	7.9
0.22	7.6	8.6
0.25	7.9	8.8

It has also been observed that all the three sols while freshly prepared give immediately transparent jellies when mixed with potassium chloride. 3 C. c. of the sols require in the case of the first sol 0.5 c. c. of *N*-KCl; while the second and third sols give jellies with 0.2 to 0.3 c. c. of *N*-KCl. After keeping the sols for 5 hours, the jelly-forming tendency appears to disappear and the coagulum is crystalline.

An investigation has also been made on the variations in conductivities of the sol on ageing.

1 G. of uric acid was suspended in 50 c.c. of conductivity water, and in one case, 0.2 g. (I) and in the second case, 0.22 g. (II) of lithium carbonate was mixed. The mixture was warmed till a clear solution was obtained. It was then cooled and filtered and the conductivities were determined at  $25^\circ \pm 0.1$ . Sol I ( $p_H$ , 7.6) and sol II ( $p_H$ , 7.6) contain 0.1965 g. and 0.2189 g. of lithium urate per 10 c.c. of the sol (Table IV).

The changes in conductivity were slow when a larger amount of lithium carbonate was used. With 0.25 g. of  $Li_2CO_3$  to 1 g. of uric acid in 50 c.c. of water, the conductivity became constant after 50 hours. The sol had an initial concentration of 0.2092 g. lithium urate per 10 c.c. and  $p_H$  7.9. The results are given in Table V.

TABLE IV.

Time.	Conductivity in mhos.	
	Sol I.	Sol II.
1 hr.	$5.516 \times 10^{-3}$	$6.219 \times 10^{-3}$
3	5.489	6.16
5	5.868	6.115
6	—	6.084

TABLE V.

Time in hour	...	...	1	5	24	29	48	58
Conductivity in mhos $\times 10^3$			6.669	6.669	6.537	6.480	5.448	5.448

In the beginning, the change in conductivity was more gradual while after about 40 hours, there is a sudden drop of conductivity to almost a constant value (Table V).

The conductivity results recorded in these tables show that the ageing of the sol is always accompanied by a decrease in the electric conductivity; the greater the alkali concentration, the slower is the change. It has always been shown that the  $pH$  of the system increases on ageing, i.e., during the decomposition of the sol, some of the hydroxyl ions are set free, and in such cases an increase in the conductivity should have been expected as has been shown by Dhar and his collaborators (*Kolloid Z.*, 1927, **42**, 120; *Z. anorg. Chem.*, 1927, **168**, 209), in the case of the ageing of sols of ferric oxide, copper ferrocyanide, thorium oxide, silicic acid or arsenious sulphide. The abnormal conductivity results of lithium urate sols support the views expressed by Schade and Boden (*loc. cit.*), or Rona and Meyer (*Biochem. Z.*, 1928, **143**, 161) who are of the opinion that about 60% of lithium urate exists as a colloid in the system and the rest as true solution, or the colloid appears to be supersaturated uric acid in which the uric acid forms an adsorption compound with the alkali. Keeser and Zocher (*Koll. Chem. Beih.*, 1928, **17**, 169), are of the view that these jelly forming urates belong to the class of electrolyte colloids. In any case, the freshly prepared lithium urate owes its high conductivity to the dissolved salt in the supersaturated state. As the ageing proceeds, the supersaturated lithium urate is removed from the system with the result that the conductivity decreases.

The jellies of lithium urate also appear to belong to the type of von Weimarn which are precipitated out from supersaturated solutions. The jelly is instantly formed and the period of gelation cannot be extended to any definite length of time. The 2% sol possesses the viscosity almost equal to that of water (0.00810 at 80°) and it does not become more viscous to any marked extent during the course of ageing or on addition of electrolytes. Thus the sol behaves as lyophobic one, and its jellies markedly differ from those obtained from lyophilic sols.

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## Chemical Examination of the Seeds of *Psoralea Corylifolia*, Linn. Part I.

By H. S. JOIS, B. L. MANJUNATH AND S. VENKATA RAO.

The plant *Psoralea corylifolia* thrives all over India and its seeds have enjoyed an honoured place in Ayurvedic medicine, particularly for the treatment of skin diseases, such as leucoderma (Nadkarni, "The Indian Materia Medica," 1927, p. 717 ; Chopra, "Indigenous Drugs of India," 1933, pp. 367-373). The seeds contain an essential oil with a persistent odour and are used locally in the preparation of certain types of medicated oils and incense preparations.

Menon (*J. Soc. Chem. Ind.*, 1910, 29, 1431) obtained the fatty oil from the seeds and determined some of its physical and chemical constants. Sen, Chatterjee and Dutta (Chopra, *loc. cit.*) in 1923, isolated an unsaponifiable oil of the formula  $C_{17}H_{24}O$  (b.p. 180-190/11-15 mm.), a yellow acidic compound ( $C_{40}H_{45}O_{11}$ ) (?) and a methylglucoside. The next chemical investigation was carried out by Chopra and Chatterjee (*Ind. J. Med. Res.*, 1927-28, 15, 49) mainly for purposes of pharmacological study and found the essential oil to be the active principle. They recommend an oleo-resinous extract for the treatment of skin diseases. The present paper contains the results of a detailed analysis of the chemical constituents of the seeds.

### *Preliminary Examination.*

50 G. of the crushed seeds were extracted successively with the following solvents and the extracts were dried at 100°.\*

Petroleum ether (b.p. 40°-60°)	...	10.86%
Ethyl ether	...	8.80
Chloroform	...	3.70
Ethyl acetate	...	3.05
Alcohol	...	8.30
		<hr/>
Total		34.70

\* The above results vary in certain respects from those recorded by Chopra and Chatterjee (*loc. cit.*).

The petroleum ether extract was found to consist of a dark reddish-brown viscous oil. The ethyl ether extract was composed mainly of the resinous constituents to which the colour of the seeds may be ascribed. No definite conclusions could be drawn regarding the nature of the constituents of the other extracts.

The seeds were tested with Prollius fluid for alkaloids. The results were negative. Alkaloidal assays by standard methods also failed to give any indication of the presence of alkaloidal constituents in the seeds. When distilled with steam, the seeds yielded 0.05% of a pale yellow volatile oil with a strong aromatic odour. An aqueous extract of the seeds gave tests for the presence of small amounts of reducing sugars and considerable amounts of hydrolysable polysaccharides. Starch and tannin were absent. Evidence was obtained regarding the presence of an enzyme in the seeds.

#### *The Petroleum Ether Extract.*

A genuine sample of the seeds was obtained from the local bazaar and 10 kg. were crushed and extracted with petroleum ether (b.p. 60-80°) in a large soxhlet. When the solvent was evaporated 1 kg. of the oil was obtained. This oil, on standing for a few days, deposited a pale yellow crystalline material (2.5% of the oil). The oil was decanted and the solid was washed with a small quantity of cold petroleum ether and purified.

The fatty oil thus obtained had the following constants.

Specific gravity	...	0.9692 at 25°
Refractive index	...	1.5182 at 25°
*Saponification value	...	117.20
Iodine value (Hanus)	...	98.9
*Acetyl value	...	96.3
*Acid value	...	19.9
Reichert-Meisel value	...	1.5
Insoluble acids (fatty acids and resin acids)	...	69.0%
Unsaponifiable matter	...	27.0%

\* These and other similar values of highly coloured substances were determined by titration in a two phase medium according to a modification of the Albert method (*Mys. Univ. J.*, 1930, 5, 241).

The oil was saponified with potassium hydroxide. The resulting soap, after extraction with ether to obtain the unsaponifiable matter, was dissolved in water and acidified with dilute hydrochloric acid, when the insoluble acids were liberated. A quantitative estimation according to Twitchell's gravimetric method showed that resin acids formed 21.5% of the mixed acids. After the removal of the resin acids, the fatty acids were separated into their saturated and unsaturated components by Twitchell's lead salt method (*Ind. Eng. Chem.*, 1921, 13, 806).

The total mixed acids had the following chemical constants.

Mean mol. wt.	...	378.6
Iodine value (Hanus)	...	108.4
<i>Insoluble fatty acids.</i>	...	78.0%
Mean mol. wt. of fatty acids	...	337.0
Iodine value (Hanus)	.	125.7
<i>Saturated fatty acids.</i>	..	18.6% of the mixed acids.
Mean mol. wt. of saturated fatty acids	..	294.5
Iodine value (Hanus)	...	3.5

The main bulk of the mixed acids was dissolved in 95% alcohol and subjected to the separation of solid and liquid acids according to the method of Twitchell, when along with the granular precipitate of the lead salts of the solid acids, most of the resin separated as a dark brown viscous mass. The granular precipitate was filtered off, washed with alcohol and ether and reprecipitated from alcoholic solution; it was thus completely freed from resin. The unsaturated acids were recovered from the alcoholic filtrates (mol. wt., 320; iodine value, 157.5).

*The unsaturated acids.*—The unsaturated acids were very highly coloured, possibly owing to the incomplete separation of resin acids. They were converted into the methyl esters and the latter distilled under reduced pressure (1 mm.), when they passed over between 168°.177° as a pale brown oil.\* A portion of the acids liberated from this was treated with bromine according to the method of Eibner and Muggenthaler (Lewkowitsch, "Chemical Technology

\* The esters were obtained in 5 different fractions whose iodine value gradually increased from 120.2 to 147.2, and the mean mol. wt. from 272 to 277 (cf. Jois and Manjunath, *J. Indian Chem. Soc.*, 1930, 7, 523).

and Analysis of Oils, Fats and Waxes", 6th Ed. Vol. I, p. 585). A small quantity of colourless ether insoluble additive compound separated. This melted at  $177-78^{\circ}$  and dissolved completely in benzene and after repeated crystallisations melted at  $188.5^{\circ}$  and proved to be hexabromostearic acid. (Found: Br, 63.4.  $C_{18}H_{30}O_2Br_6$  requires Br, 63.8 per cent). This indicated the presence of a small amount of linolenic acid in the unsaturated acids. From the ether soluble additive compounds tetrabromostearic acid (m.p.  $113-14^{\circ}$ ) was isolated.

Another portion of the mixed liquid acids from the methyl esters was oxidised by cold dilute alkaline permanganate and from the mixture of insoluble hydroxy acids dihydroxystearic acid (m.p.  $130-31^{\circ}$ , mol. wt. 316.4) and tetrahydroxystearic acid (m.p.  $156^{\circ}$ , mol. wt. 348.4) were isolated. From the mother liquors of the oxidation mixture a small quantity of hexahydroxystearic acid (m.p.  $173^{\circ}$ , mol. wt. 381.5) was obtained.

The above results establish the presence of oleic and linolic acid and a small quantity of linolenic acid among the unsaturated acids.

*The saturated acids.*—The solid acids, obtained by Twitchell's method of separation were slightly coloured. They were converted into the methyl esters (50 g.) and fractionally distilled at 1 mm. pressure.

Fraction No.	Range of Temperature.	Wt. of fraction.	Mean mol. wt. of acids from the saponification value.
1	150–152°	22.80	251.4
2	152–155°	4.46	255.4
3	155–158°	1.10	256.5
4	158–162°	4.00	266.7
5	162–164°	0.55	268.0
6	164–172°	3.45	271.8
7	172–181°	1.23	277.4
8	181–182°	1.69	280.3
9	Residue	10.10	362.0

Pure palmitic acid (m. p.  $61^{\circ}$ , mol. wt. 257.8) was isolated from the first three fractions. Its *p*-phenylphenacyl ester was

prepared according to Drake and Bronitsky (*J. Amer. Chem. Soc.*, 1930, **52**, 3715) and was found to melt at 94°. (Found: C, 80·07; H, 9·21.  $C_{30}H_{42}O_3$  requires C, 79·95; H, 9·4 per cent).

From fractions 4 to 7 about 2 g. of pure stearic acid (m.p. 68·4°, mol. wt. 285·1) was isolated. Its *p*-phenylphenacyl ester melted at 97·5°. (Found: C, 80·37; H, 9·71.  $C_{32}H_{46}O_3$  requires C, 80·26; H, 9·69 per cent). The mother liquors of stearic acid gave a fraction melting at 58-59° having the mol. wt. 263.

The residue (9) was highly coloured. It was saponified and the liberated acid was treated with animal charcoal and crystallised from 95% alcohol. It melted at 75-76° and had the mol. wt. 368·1. It did not depress the m.p. of a pure sample of lignoceric acid from another source. Repeated recrystallisations from various solvents did not raise the melting point. An attempt to obtain a specimen having a higher m.p. by the partial precipitation of the lithium salt according to Holde and Godbole (*Ber.*, 1926, **59**, 39) was unsuccessful. Its identity was confirmed by comparing its *p*-phenylphenacyl ester with that of pure lignoceric acid melting at 102°. (Found: C, 81·14; H, 10·4.  $C_{38}H_{58}O_3$  requires C, 81·07; H, 10·39 per cent).

The unsaponifiable matter consisted of a dark brown viscous mass and contained principally neutral resin bodies. However, it gave the colour reactions of sterols but no pure compound could be isolated even by digitonin treatment.

The crystalline solid, deposited on keeping the oil for some time, was found to melt at 135° (*cf.* Chopra and Chatterjee, *loc. cit.*). From this material on repeated crystallisations from dilute alcohol a pure compound melting at 102° was isolated as the main constituent. This substance was found to have the formula  $C_{11}H_6O_3$ . [Found: C, 71·01; H, 3·20. M. W. (in benzene by the cryoscopic method), 182.  $C_{11}H_6O_3$  requires C, 70·94; H, 3·25 per cent; M. W., 180). It has been named *Psoralen*.

*Psoralen* is sparingly soluble in cold petroleum ether and ether but dissolves readily in alcohol and chloroform. It can be crystallised in long silky needles from boiling water in which it is slightly soluble. It is insoluble in cold dilute sodium carbonate or sodium hydroxide, but when heated dissolves readily. The material is precipitated unchanged on acidifying. Preliminary investigations have indicated that it is possibly a coumaron-coumarin. Further work is in progress regarding its constitution and the results will be communicated in a subsequent paper.

## SUMMARY.

The petroleum ether extract of the seeds of *Psoralea corylifolia* gave a dark reddish-brown oil and a crystalline solid  $C_{11}H_8O_3$  now named *Psoralen*, melting at  $162^\circ$ . The oil was found to contain a considerable amount of resin. The fatty acids obtained from the oil were found to be principally palmitic, oleic and linolic acids together with small amounts of stearic, lignoceric and linolenic acids.

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## Derivatives of Salicylic Acid. Part IV. Synthesis and Constitution of 4-Sulphosalicylic Acid.

BY NARHAR WAMAN HIRWE AND MOHINIRAM RAJARAM JAMBHEKAR.

Of the four possible sulphosalicylic acids, 5-sulphosalicylic acid was the only one known for a long time, being the sole product of direct sulphonation (Mendius, *Annalen*, 1857, 103, 45 ; Remsen, *ibid.*, 1875, 179, 107 ; Hirsch, *Ber.*, 1900, 33, 3239 ; Meldrum and Shah, *J. Chem. Soc.*, 1923, 123, 1986). The synthesis of 3-sulphosalicylic acid was worked out by Hirwe (*J. Indian Chem. Soc.*, 1930, 7, 893). The aim of the present work was to synthesise and confirm the constitution of 4-sulphosalicylic acid.

Since the 4-position in the salicylic acid nucleus is not favoured by the directing influences, an indirect synthesis only is possible. 2-Nitrotoluene-4-sulphonic acid was chosen as the starting substance.

It was obtained by the (1) nitration of toluene-4-sulphonic acid or by the (2) sulphonation of *o*-nitrotoluene.

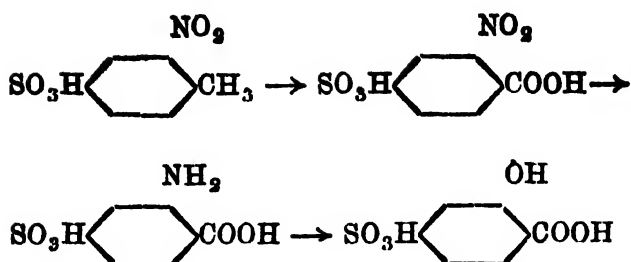
Fichter and Bernoulli (*Ber.*, 1909, 42, 4309) prepared sodium 2-nitrotoluene-4-sulphonate by the nitration of sodium toluene-4-sulphonate with a mixture of nitric and sulphuric acids. They did not try to get the free acid. Instead of sulphuric acid we used acetic anhydride during nitration and obtained the free acid directly.

The acid was also prepared by the sulphonation of 2-nitrotoluene (Beilstein and Kuhlberg, *Annalen*, 1870, 155, 27 ; Kornatzki, *ibid.*, 1883, 221, 180). The acid was isolated as potassium salt, which was converted into the barium salt from which the free acid was liberated in the usual way.

The compounds produced by both the methods are identical, which confirms the constitution as 2-nitrotoluene-4-sulphonic acid.

4-Sulphosalicylic acid was obtained from the above by first oxidising the methyl group to carboxyl, then reducing the nitro group and finally converting the amino group to hydroxyl in the usual way.

The position of the sulphonic acid group in the compound is established by its conversion to  $\beta$ -resorcylic acid (m. p. 208°), when fused with caustic potash,



## EXPERIMENTAL.

**2-Nitrotoluene-4-sulphonic acid.** *Method I.*—Toluene-*p*-sulphonic acid (50 g.) was dissolved in acetic anhydride (150 c.c.) and the solution cooled in ice. To this cold solution nitric acid (36 c.c., *d* 1.41) was slowly added, keeping the temperature below 10°. The flask was corked and kept at room temperature for 48 hours, and then the mixture was poured in a crystallising basin and kept in a vacuum desiccator over alkali to get rid of the excess of nitric acid and the acetic anhydride, when a solid was obtained. It was recrystallised from a small amount of water as long pale yellow needles. It is very hygroscopic and so was kept overnight in an alkali desiccator; m.p. 92° and decomposes at 245°, yield 92 p. c. (Found: N, 5.61; S, 12.69; Eq. wt., 262.9.  $\text{C}_7\text{H}_7\text{O}_5\text{NS}$ , 2  $\text{H}_2\text{O}$  requires N, 5.63; S, 12.64 per cent; Eq. wt., 253.1).

*Method II.*—Beilstein and Kuhlberg (*loc. cit.*) have isolated the barium salt. The potassium salt, however, can be easily and conveniently prepared in good yields by potassium chloride solution.

**Potassium 2-nitrotoluene-4-sulphonate** was prepared from the acid by neutralising with potassium carbonate. It is moderately soluble in water, from which it crystallises in greyish white needles. (Found: K, 16.80.  $\text{C}_7\text{H}_6\text{O}_5\text{NSK}$  requires K, 16.51 per cent). The composition of the sodium salt ( $\text{C}_7\text{H}_6\text{O}_5\text{NSNa}$ ,  $\text{H}_2\text{O}$ ) agrees with that of Fichter and Bernoulli (*loc. cit.*) and that of the barium salt [ $\text{C}_7\text{H}_6(\text{NO}_2)\text{SO}_3$ ]<sub>2</sub>Ba, 2 $\text{H}_2\text{O}$  with that of Beilstein and Kuhlberg (*loc. cit.*).

**Acid potassium 2-nitro-4-sulphobenzoate.**—Potassium-*o*-nitrotoluene-*p*-sulphonate (45 g.) was mixed with a cold concentrated solution of potassium permanganate (60 g.) and a cold solution of potassium hydroxide (25 g.) was added to it. The mixture was shaken from time to time and the oxidation was carried out at room temperature, which requires about 6 days. Boiling with potassium permanganate



(cf. Hart, *J. Amer. Chem. Soc.*, 1879, 1, 352) decomposes a part of the substance and affects the yield. On completion of the oxidation the mixture was filtered and the filtrate acidified with HCl to get the acid potassium salt. It was recrystallised from hot water, in which it is easily soluble, as needles. On slow crystallisation it was obtained in transparent hexagonal plates. Yield 87 per cent.

The potassium salt was converted into the neutral barium salt, which is difficultly soluble in boiling water, and crystallises from it in yellowish grains with two molecules of water of crystallisation, which can be completely removed only at 180° under reduced pressure.

The compositions of the acid potassium salt as well as of the neutral barium salt agree with those given by Hart (*loc. cit.*).

2-Nitro-4-sulphobenzoic acid was obtained by digesting the barium salt with the calculated amount of dilute sulphuric acid. A solid was obtained on evaporating the filtrate to dryness. It was recrystallised from water as small white needles, m.p. 111°. It is very hygroscopic and so was kept in a desiccator over calcium chloride overnight and then analysed (Found: N, 4·95; S, 11·05; Eq. wt., 145·8.  $C_7H_5O_7NS$ ,  $2\frac{1}{2} H_2O$  requires N, 4·79; S, 10·96 per cent; Eq. wt., 146·0).

Acid dichloride of 2-nitro-4-sulphobenzoic acid,  $[C_6H_3(NO_2)-(SO_2Cl)(COCl)]$  was prepared by heating on a boiling water-bath a mixture of acid potassium nitrosulphobenzoate (10 g.) and phosphorus pentachloride (30 g.). The mixture was poured over ice and stirred, when a solid was obtained which is very easily soluble in cold benzene. It was recrystallised from benzene in clusters of small needles, yield 10 g. It softens at 145° and melts at 160°. (Found: N, 4·98; Cl, 24·88; S, 11·24.  $C_7H_3O_5NCl_2S$  requires N, 4·98; Cl, 24·97; S, 11·29 per cent).

Acid amide of 2-nitro-4-sulphobenzoic acid.—The dichloride was mixed with ammonium hydroxide (*d* 0·880) and on concentrating a solid was obtained. It crystallised from water as white needles, m.p. 228°. (Found: N, 17·13; S, 18·20.  $C_7H_7O_5N_3S$  requires N, 17·14; S, 18·06 per cent).

Acid monochloride of 2-nitro-4-sulphobenzoic acid.—A solid was obtained by shaking the acid dichloride with cold water for about 2 hours. It is fairly soluble in boiling benzene and toluene. It softens at 192° and decomposes at 202°. If long shaken with water it hydrolyses further into nitrosulphobenzoic acid. (Found: Cl, 18·45.  $C_7H_4O_6NClS$  requires Cl, 18·88 per cent).

*4-Sulphonamide-2-nitrobenzoic acid* is obtained in two different ways *vis.*, (1) by refluxing the diamide (3 g.) for about 4 hours with concentrated hydrochloric acid (50 c.c.) and (2) by the action of ammonium hydroxide (*d* 0.880) on the acid monochloride. It crystallises in needles from water, m.p. 192°. (Found: N, 11.61; S, 13.15.  $C_7H_6O_6N_2S$  requires N, 11.89; S, 13.01 per cent).

*4-Sulphoanthranilic acid*.—A free acid was obtained by reducing acid potassium 2-nitro-4-sulphobenzoate (10 g.) dissolved in concentrated hydrochloric acid by tin (15 g.). On cooling a solid separates, which is dissolved in water and neutralised with sodium carbonate solution and filtered. The filtrate gave the sulphoanthranilic acid on acidification, yield 7 g. It crystallises as tiny greyish white needles from boiling water. It gives a blue fluorescence in very dilute solutions. (Found: N, 6.19; S, 13.82; Eq. wt., 118.1.  $C_7H_7O_5NS$ ,  $H_2O$  requires N, 5.96; S, 13.60 per cent; Eq. wt., 117.5).

*Barium 4-sulphoanthranilate* is soluble in water and crystallises in granules and gives blue fluorescence in dilute solutions. (Found: Ba, 38.76.  $C_7H_5O_5NSBa$  requires Ba, 38.92 per cent).

*4-Sulphoanthranilamide* was obtained by the reduction of monoamide of 2-nitro-4-sulphobenzoic acid with alcoholic ammonium sulphide. It crystallises from water in needles, m.p. 227-28° and shows a blue fluorescence in dilute solutions. (Found: S, 14.94.  $C_7H_8O_4N_2S$  requires S, 14.81 per cent).

*1-Carboxy-2-diazobenzene-4-sulphonate*.—4-Sulphoanthranilic acid (30 g.) was suspended in dilute hydrochloric acid and potassium nitrite (10 g.) was slowly added. When the addition was complete the mixture was cooled to 0° and the separated solid filtered and washed with ice-cold water. It is a grey white powder decomposing at 163-64°, yield 24 g. (Found: Eq. wt., 246.5.  $C_7H_4O_5N_2S$ ,  $H_2O$  requires Eq. wt., 246.0).

*4-Sulphosalicylic acid*.—The above diazo compound was heated on a water-bath with dilute hydrochloric acid for a time and the solution then evaporated to dryness. The solid was crystallised from water in needles with 3 molecules of water of crystallisation, m. p. 82° (air-dried). It loses 1 molecule of water when left over sulphuric acid and melts at 133°. It gives an intense violet coloration with ferric chloride. It is hygroscopic and its deliquescence depends upon the humidity of the atmosphere. [Found: (desiccated substance) S, 12.74; Eq. wt., 125.7.

$C_7H_6O_6S$ ,  $2H_2O$  requires S, 12.60 per cent ; Eq. wt., 127). Found : (air-dried substance), S, 11.80 ; Eq. wt., 135.8.  $C_7H_6O_6S$ ,  $8H_2O$  requires S, 11.76 per cent ; Eq. wt., 136.0].

*Acid sodium 4-sulphosalicylate* crystallises from water with 2 molecules of water of crystallisation. (Found : Na, 8.10;  $H_2O$ , 18.39 ; Eq. wt., 275.8.  $C_7H_5O_6SNa$ ,  $2H_2O$  requires Na, 8.33 ;  $H_2O$ , 18.04 per cent ; Eq. wt., 276).

*Acid potassium 4-sulphosalicylate* crystallises from water in yellow needles, less soluble in water than the sodium salt. (Found : K, 15.27.  $C_7H_5O_6SK$  requires K, 15.24 per cent).

*Barium 4-sulphosalicylate* is insoluble in cold and difficultly soluble in hot water from which it crystallises in pale reddish plates with 4 molecules of water. (Found : Ba, 32.32 ;  $H_2O$ , 12.96.  $C_7H_4O_6SBa$ ,  $4H_2O$  requires Ba, 32.23 ;  $H_2O$ , 12.71 (with  $3H_2O$ ) per cent. The last molecule of water could not be removed and so the salt after the removal of 3 molecules of water was analysed again. (Found : Ba, 37.13.  $C_7H_4O_6SBa$ ,  $H_2O$  requires Ba, 36.83 per cent).

*Calcium 4-sulphosalicylate* is soluble in water. (Found : Ca, 10.91.  $C_7H_4O_6SCa$ ,  $6H_2O$  requires Ca, 10.99 per cent).

The position of the sulphonic acid group in the sulphosalicylic acid was definitely established by potash fusion of its acid potassium salt for 15 minutes at  $230-40^\circ$  in the usual way, when  $\beta$ -resorcylic acid, identified by mixed melting point, was obtained.



# **The Influence of Non-electrolytes on the Coagulation of Ceric Hydroxide Sol Dialysed to Different Extent.**

BY MATA PRASAD AND M. V. NABAR.

It has generally been observed that the coagulating concentration of ions for a sol decreases in the presence of some non-electrolytes and increases in the case of others. The sensitisation of sols by non-electrolytes has been observed by Billitzer (*Z. physikal. Chem.*, 1903, **48**, 312), Freundlich and Rona (*Biochem. Z.*, 1917, **81**, 87), Weiser (*J. Phys. Chem.*, 1924, **28**, 1253), Dhar and collaborators and others.

Desai (*Trans. Faraday Soc.*, 1928, **34**, 181), has pointed out that the stability of the colloidal thorium hydroxide decreases as the sol is continuously dialysed. The sensitisation or the protection of the colloid by the non-electrolytes will, therefore, be more prominent as the sol becomes purer. Patel and Desai (*Kolloid Z.*, 1930, **81**, 318) have found that the sensitising influence of alcohols, acetone, urea and sugars increases with the progress of the dialysis of the thorium hydroxide sol and that a pure sol can be coagulated by non-electrolytes alone. In this investigation the influence of non-electrolytes on the coagulation of ceric hydroxide sol by electrolytes has been studied and the effect of the dialysis of the sol on such an influence has also been examined.

## **EXPERIMENTAL.**

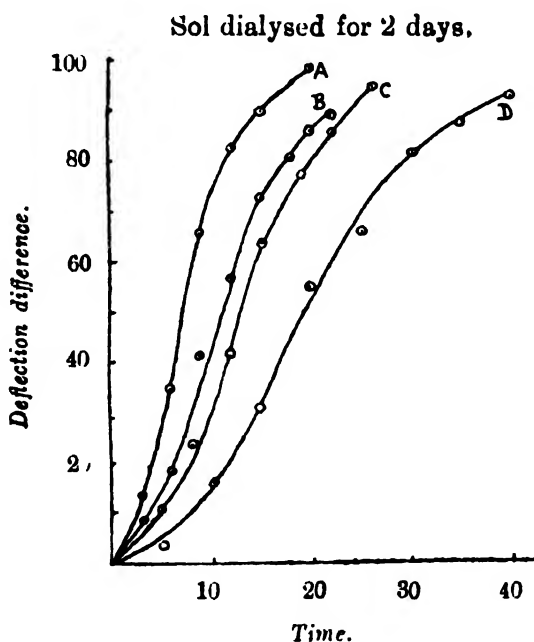
5 C. c. of the colloid were taken in a test tube and in another a solution of NaCl, made up to 7 c. c. by adding distilled water, of such concentration as to completely coagulate the sol in 30-40 minutes. The contents of the two test tubes were mixed together a fixed number of times and the time of mixing was noted. The coagulation velocity of the sol was followed by the thermopile method.

Next, the same amount of NaCl as used in the previous experiments was made up to 7 c.c. by adding different volumes of non-electrolytes and water. This was mixed (the mode of mixing being the same as used in the previous experiment) with 5 c. c. of the sol and the coagulation velocity was followed in the same manner as before,

The non-electrolytes used were methyl, propyl and amyl alcohols, and solutions of glucose and sucrose. Merck's extra pure alcohols were further purified by refluxing and distilling over metallic calcium. Sugars used were Merck's extra pure chemicals. The sol was prepared and dialysed in the same way as described in the previous paper (*J. Indian Chem. Soc.*, 1932, 9, 609).

The deflection differences were plotted against time and the curves obtained for the coagulation of the sol dialysed for two days in the presence of alcohols and sugars are shown in Figs. 1 and 2

FIG. 1.



A—1 c. c.  $\text{CH}_3\text{OH}$ ; B—1 c.c.  $\text{C}_3\text{H}_7\text{OH}$ ;  
C—1 c. c.  $\text{C}_5\text{H}_{11}\text{OH}$ ; D— $\text{NaCl}$ .

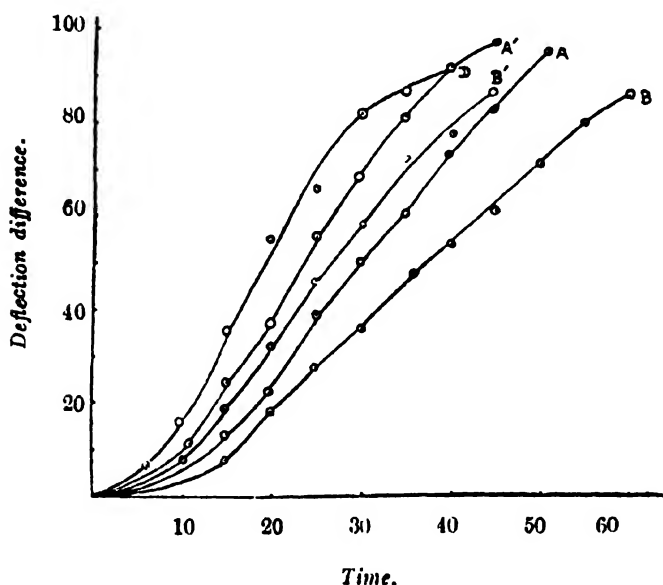
respectively. The inclination of the curves in Fig. 1 shows that the addition of alcohols to a solution of sodium chloride increases the coagulation velocity of the sol and this effect increases as the amount of alcohol is increased. The order of the effectiveness of the alcohol is  $\text{CH}_3\text{OH} > \text{C}_3\text{H}_7\text{OH} > \text{C}_5\text{H}_{11}\text{OH}$ , the same as observed by Mukherjee and collaborators (*J. Indian Chem. Soc.*, 1928, 5, 697).

The coagulation velocity curves with the same amount of alcohol for sol dialysed for 10 days are steeper than those for the sol dialysed for 6 days. This shows that the sensitising action of the alcohols on the sol becomes more pronounced as it becomes purer.

It was also observed that the sol dialysed for 10 and 16 days could be coagulated by alcohols alone, the amount of alcohol required for the same volume of the latter sample was smaller than that for the former. On the addition of alcohol to these samples, the sol either coagulated immediately, or did not coagulate at all, if the quantity of alcohol added was insufficient, but no slow coagulation was observed.

FIG. 2.

Sol dialysed for 2 days.



A and A'—1 c. c. and 0.5 c. c. of M/10-glucose;  
 B and B'—1 c. c. and 0.5 c. c. of M/10-sucrose;  
 D—NaCl.

Fig. 2 shows that sugars exert a protective action on the sol. These results do not support the observation of Patel and Desai (*loc. cit.*) who find that sugars sensitise the thorium hydroxide sol. The protecting influence of sugars on ceric hydroxide sol increases with the progress of dialysis of the sol and with an increase in the amount of sugar added to the sol. The sol dialysed for different days could be coagulated by the same amount of the sodium chloride in the presence of the same amount of glucose but the protection is greater as the sol gets purer. But if the amount of cane sugar added to the sol dialysed for 2 days is mixed with the sol dialysed for 6 and 10 days, no coagulation with the same amount

of sodium chloride takes place. This observation and the curves in Fig. 2 show that cane sugar is a better protective agent than glucose, probably because of the greater number of hydroxyl groups contained in it.

The sensitising action of alcohols cannot be explained by the diminution in the adsorption of the coagulating ion by the ceric hydroxide particles as suggested by Weiser (*loc. cit.*) as in that case the slow coagulation will be observed and coagulation velocity curves may be 'S' shaped. But as the sensitising effect of the alcohols increases as the sol gets purer, the second view of Weiser (*loc. cit.*) that the non-electrolytes displace the stabilising ion from the colloidal particles may apply to this case.

Also the addition of alcohols to the sol lowers its dielectric constant and decreases the density of charge on the colloidal particles. Hence the increased rate of coagulation of the sol by mixtures of alcohols and sodium chloride than by sodium chloride alone may be due to the fall in the potential of the particles. The steepness of the coagulation velocity curves is, however, further increased as the sol is dialysed and the potential of the particles is lowered due to the removal of the stabilising ions. When the sol gets almost pure, the potential of the colloidal particles is fairly low, and the addition of alcohol alone causes a further lowering and therefore the coagulation of the colloid.

The protecting action of the sugars in ceric hydroxide sol may, however, be due to the well known peptising influence of sugars.

#### SUMMARY.

(1) The coagulation velocity of ceric hydroxide sol has been studied with a mixture of an electrolyte and non-electrolyte with progress of dialysis.

(2) It is found that alcohols sensitise the sol while sugars protect it. The order of the effect of alcohols in their sensitising action is  $\text{CH}_3\text{OH} > \text{C}_3\text{H}_7\text{OH} > \text{C}_5\text{H}_{11}\text{OH}$ .

(3) Cane sugar acts as a better protecting agent than glucose.

(4) As the sol gets purer and purer, the sensitising action of the alcohols and the protective action of sugars also increase.

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## A Note on the Minimal Critical Pressure of Explosions.

By K. S. GURURAJA DOSS.

In order to explain the variation of the minimal critical pressure with temperature, Semenoff (*Z. Physik*, 1928, **48**, 571 ; *Chem. Rev.*, 1929, p. 347 ; Taylor, "A Treatise on Physical Chemistry" p. 101f) has proposed two theories. It is attempted in this paper to point out an error that has crept in the development of the first theory and to show the relationship between the two theories.

In his first theory, Semenoff derives the marginal condition for an explosion the relation :

$$\frac{KRT_2^a}{E} = K(T_2 - T_0) = B. \quad e^{-E/RT_2} \quad n_1^a \quad n_2^b \quad \dots \quad (1)$$

where  $T_0$  = the temperature of the walls,  $T_2$  = the temperature of the reaction mixture,  $E$  = the energy of activation,  $R$  = the gas constant,  $K, B$  = constants,  $n_1, n_2$  = the concentrations of the reactants and  $a, b, \dots$  = the numbers corresponding to the orders of the reaction with reference to the reactants.

From this equation semenoff derives,

$$T_2 = T_0 \left( 1 - \frac{RT_0}{E} \right)$$

which is incorrect. The correct expression for  $T_2$  is

$$T_2 = \frac{E}{2R} \left\{ 1 \pm \sqrt{1 - \frac{4RT_0}{E}} \right\} \quad \dots \quad (2)$$

which gives, on taking the minus sign,  $T_2 = T_0 \left( 1 + \frac{RT_0}{E} \right)$  to a close approximation. This means that  $T_2 \approx T_0$  as  $RT_0$  is small as compared with  $E$ . It can be so only if the heat of the reaction is small. As the explosive reactions are usually highly exothermic, this

solution for equation (2) has to be discarded. Taking the positive solution, we get,

$$T_2 = \frac{E}{R} \left( 1 - \frac{RT_0}{E} \right)$$

to a close approximation.

Substituting the value of  $T_2$  in equation (1) and setting

$$n_1 = \alpha n_0 \cdot \frac{P}{T_2} \cdot \frac{273}{760} ; n_2 = \beta n_0 \cdot \frac{P}{T_2} \cdot \frac{273}{760} ; \dots \dots \dots$$

where  $n_0$  = the total pressure at S.T.P.

and  $\alpha, \beta \dots$  = the mole fractions of the different reactants, and taking logarithms of both sides, we get,

$$\begin{aligned} (a+b+\dots) \ln p = & \underbrace{-\ln \left\{ B \alpha^a \beta^b \dots \left( n_0 \frac{273}{760} \right)^{a+b+\dots} \cdot \frac{R}{KE} \right\}}_{\text{constant}} \\ & + \underbrace{\frac{RT_0}{E} + 1 + (a+b+\dots) \ln \left[ \frac{E}{R} \left\{ 1 - \frac{RT_0}{E} \right\} \right]}_{\text{practically constant}} + \underbrace{\ln \left( 1 - \frac{2RT_0}{E} \right)}_{\text{negligible}} \end{aligned}$$

Thus  $P$  = a constant.

So, on the basis of the first theory, the minimal critical pressure must be independent of temperature (the incorrect expression leads to the conclusion that the minimal critical pressure is related to the temperature by the equation  $\ln P = A + B/RT_0$  where  $A$  and  $B$  are some constants).

This also becomes evident by a consideration of the relationship between the two theories. In the first theory the temperature equilibrium is assumed to take place. In the marginal state

$$T_2 = \frac{E}{R} \left\{ 1 - \frac{RT_0}{E} \right\} \text{ or } RT_2 \cong E \text{ as } RT_0 \text{ is small.}$$

Let us interpret in terms of the second theory. The heat of the reaction which has occurred so far is large enough to raise the temperature of the whole mixture to such a degree as to have a molecule

possessing average energy in the activated state. At this stage  $U$ , the minimum energy that is expected of a reactant molecule to get activated by a collision of the second kind with the product molecule, is very small as compared with  $RT$ ; hence in the equation (derived on the basis of the second theory)

$\ln P = A + \frac{U}{nRT}$ , we can put  $\frac{U}{nRT} = 0$ . Hence, we get,  $P = \text{a constant}$ .

Thus a 'thermal' explosion (as pictured in the first theory) corresponds to a 'chain' explosion (as envisaged in the second theory) with a low value for  $U$ .

#### SUMMARY.

An error in the development of the first theory of Semenov is pointed out.

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*Received November 22, 1932.*



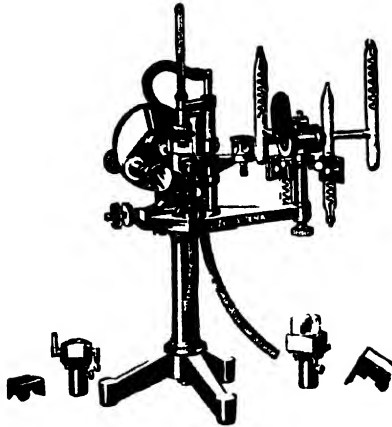
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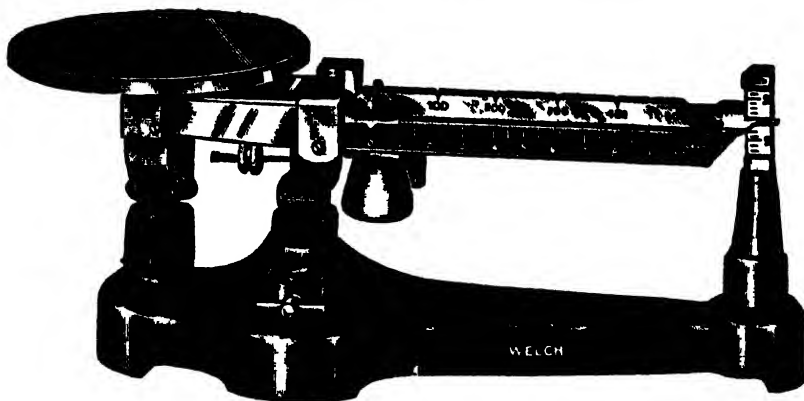


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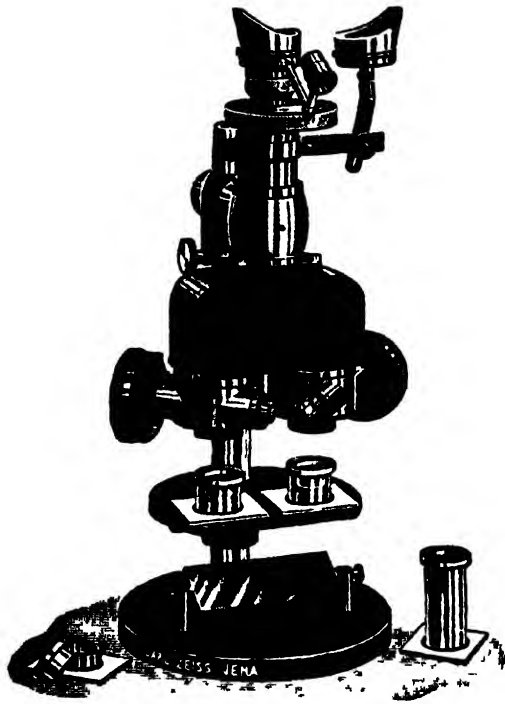
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# Studies in the Coagulation of Colloids from the Standpoint of Smoluchowski's Theory. Part IV. Variation of the Surface Tension during the Coagulation of the Manganese Dioxide Sol.

BY SHRIDHAR SARVOTTAM JOSHI AND AVADH NARAYAN LAL.

It was observed in Part II (*J. Indian Chem. Soc.*, 1931, 8, 377) and Part III (*ibid.*, 1932, 9, 157) of this series, that in the *slow* coagulation of the arsenious sulphide sol by dilute sulphuric acid, the departure from the requirements of Smoluchowski's theory (as shown by the diminution in  $\beta$ ) occurred in all the cases, examined during the initial stages of coagulation. In view of its unexpected character, it was thought desirable to investigate the above conclusion employing a method of measuring coagulation, different from that used previously (*loc. cit.*).

## EXPERIMENTAL.

The manganese dioxide sol was prepared by Cuy's method (*J. Phys. Chem.*, 1921, 25, 415; also *cf.* Joshi and Narayan, *J. Indian Chem. Soc.*, 1930, 7, 883) and stocked in well cleaned silica vessels. The sol contained a small amount of potassium hydroxide which was found to be necessary for its stability. The colloid content of the sol was determined by treating a known volume of the sol with a known volume of standard oxalic acid solution, acidified with dilute sulphuric acid. The progress of the coagulation was followed by measuring the surface tension of the coagulating sol by means of a stalagmometer. The sol was so dilute that its density was found to be practically the same as that of water. The values of the surface tension of the sol, relative to that of water taken as unity, were obtained, therefore, from a knowledge of the significant drop numbers only. Coagulations were also studied when suitable amounts of solutions of sodium oleate and of sugar were added to the sol, before the addition of the coagulator solution. Two principal series of coagulation were studied. In the first, KCl in different concentrations was the coagulator; in the other  $\text{BaCl}_2$  was used. In any given series, to a fixed volume of the sol,

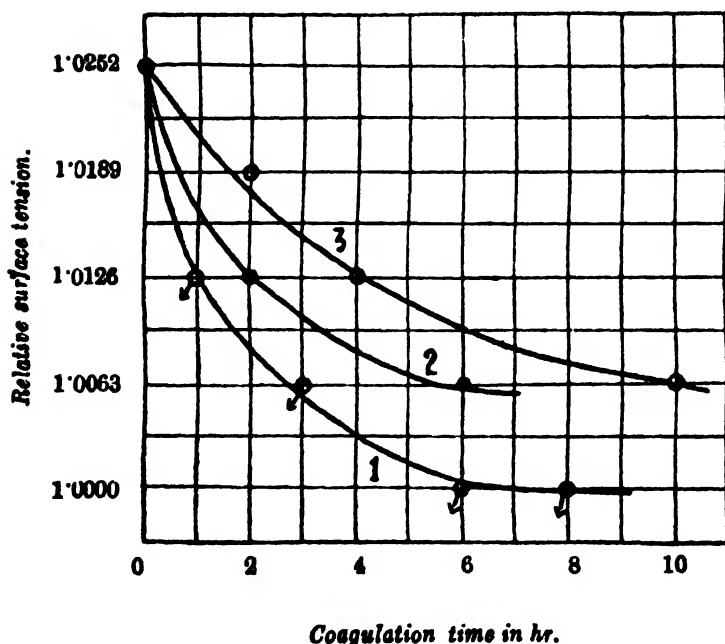
varying amount in c. c. of the coagulator solution of a definite concentration and such amounts of water were added so that the volume of the coagulating mixture was always constant. These values for any given coagulation are cited in reference to the corresponding coagulation-time curve in Figs. 1—7. The concentrations of the protector, the coagulator solution, and of the colloid shown in the following results refer to their values before mixing for coagulation. The colloid concentration was 0.87 g.  $\text{MnO}_2$  per litre in all these cases (that is, in Figs. 1—3, and 6, 7). Figs. 4 and 5 refer to coagulations by  $\text{BaCl}_2$  and  $\text{KCl}$  respectively of a sol containing 0.695 g.  $\text{MnO}_2$  per litre. The mode of getting the  $\beta$ -time curves in Figs. 4—6 and of data in Tables I—V is explained later.

#### DISCUSSION.

These results show that except when sodium oleate was added (cf. Fig 7, curves 1, 2) the surface tension of the coagulating sol

FIG. 1.

Coagulation by  $\text{KCl}$  (0.87 g.  $\text{MnO}_2$  per litre).

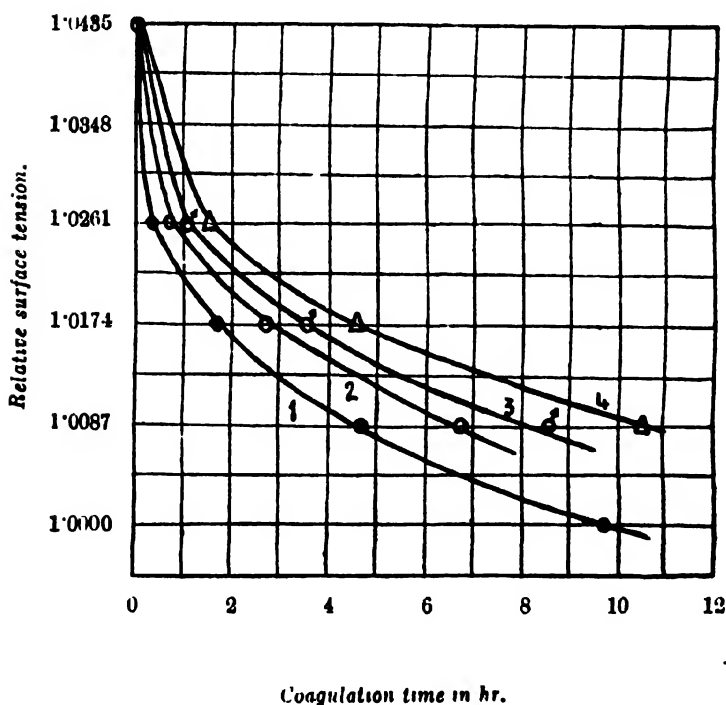


- Curve 1—20 c. c. of the sol + 4 c. c.  $M/1000\text{-BaCl}_2$ .
- Curve 2— „ „ + 2 c.c. „ „ + 2 c. c.  $\text{H}_2\text{O}$ .
- Curve 3— „ „ + 1 c.c. „ „ + 1 c. c.  $\text{H}_2\text{O}$ .

diminishes continuously during the progress of coagulation (*cf.* Figs. 1—3; curves A, B, in Fig. 4 and curves C, D in Fig. 5). The greater coagulating power of  $\text{BaCl}_2$  than  $\text{KCl}$  is clearly brought out by comparing the curves in Figs. 1 and 2. A comparison of curves in Figs. 2 and 3 shows that the influence of the addition of sugar is not appreciable on the progress of the coagulation of the sol. In view of the usual (though not invariable) relationship between the adsorbability of a substance and its influence as a coagulant, it is interesting in this case to observe that Bhatnagar, Shrivastav and Gupta (*Kolloid Z.*, 1925, 37, 101) observed that sugar is not adsorbed sensibly by manganese dioxide.

FIG. 2.

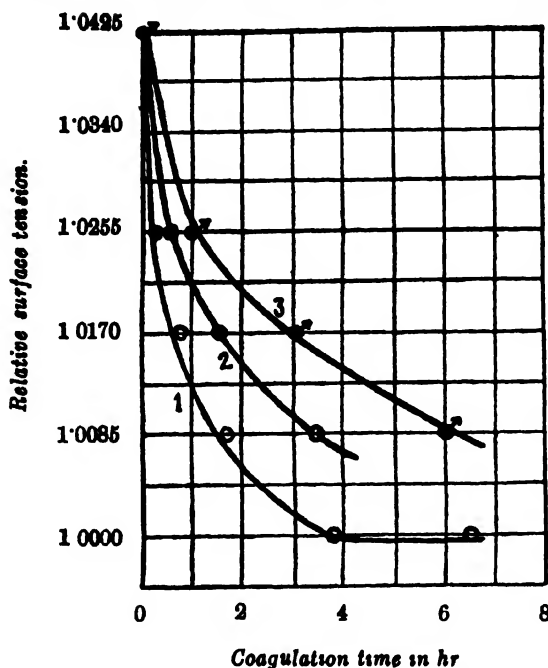
Coagulation by  $\text{BaCl}_2$  (0.87g.  $\text{MnO}_2$  per litre).



Curve 1—20 c. c. sol + 4 c.c.  $\text{M}/1000\text{-KCl}$  + 0 c. c.  $\text{H}_2\text{O}$   
 Curve 2— „ „ + 3 „ „ + 1 „ „  
 Curve 3— „ „ + 2 „ „ + 2 „ „  
 Curve 4— „ „ + 1 „ „ + 3 „ „

FIG. 8.

Coagulation by  $\text{BaCl}_2$  in presence of sugar (0.87g.  $\text{MnO}_2$  per litre).



Curve 1—20 c.c. sol. + 4 c.c. sugar soln + 4 c.c.  $M/-1000 \text{ BaCl}_2$   
 Curve 2— " " + " + 2 + 2 c.c.  $\text{H}_2\text{O}$   
 Curve 3— " " + " + 1 + 3 "

Sugar soln. (5.5 g. in 100 c. c.)

In the previous papers in this series results are given of the application of Smoluchowski's theory to the coagulations of colloid antimony sulphide (Part I, *J. Indian Chem. Soc.*, 1931, 8, 11), and of arsenious sulphide (Part II, *loc. cit.*, Part III, *loc. cit.*). The following equation was used (Part I)

$$\beta = \frac{1}{t} \left[ \sqrt{\frac{n_0}{n_t}} - 1 \right] \quad \dots \quad \dots \quad \dots \quad (i)$$

$n_0$  and  $n_t$  denote here the number of primaries at time,  $t=0$ , and  $t=t$ , respectively. The quantity  $n_t$ , the number of primaries in the system diminishes with the progress of coagulation. It is now assumed that  $n_t$  at any given time during coagulation is proportional to the reciprocal of the surface tension of the coagulating sol. The quantity  $n_0/n_t$  is thus obtained, and  $\beta$  can therefore be calculated from (i), curves *a*, *b* in Fig. 4, curves *c*, *d* in Fig. 6 and Fig. 6 show the variation of  $\beta$  during the various coagulations.

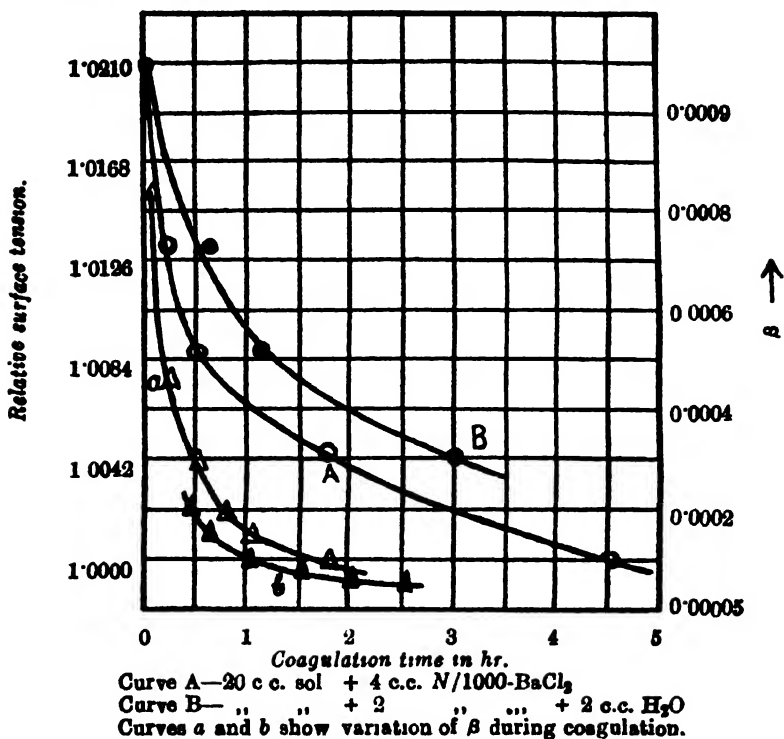
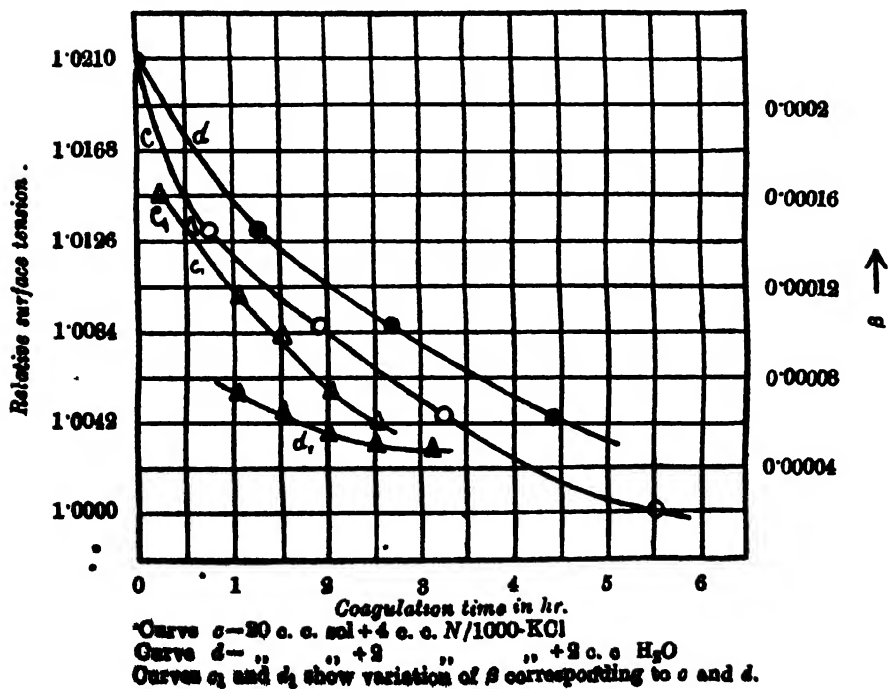
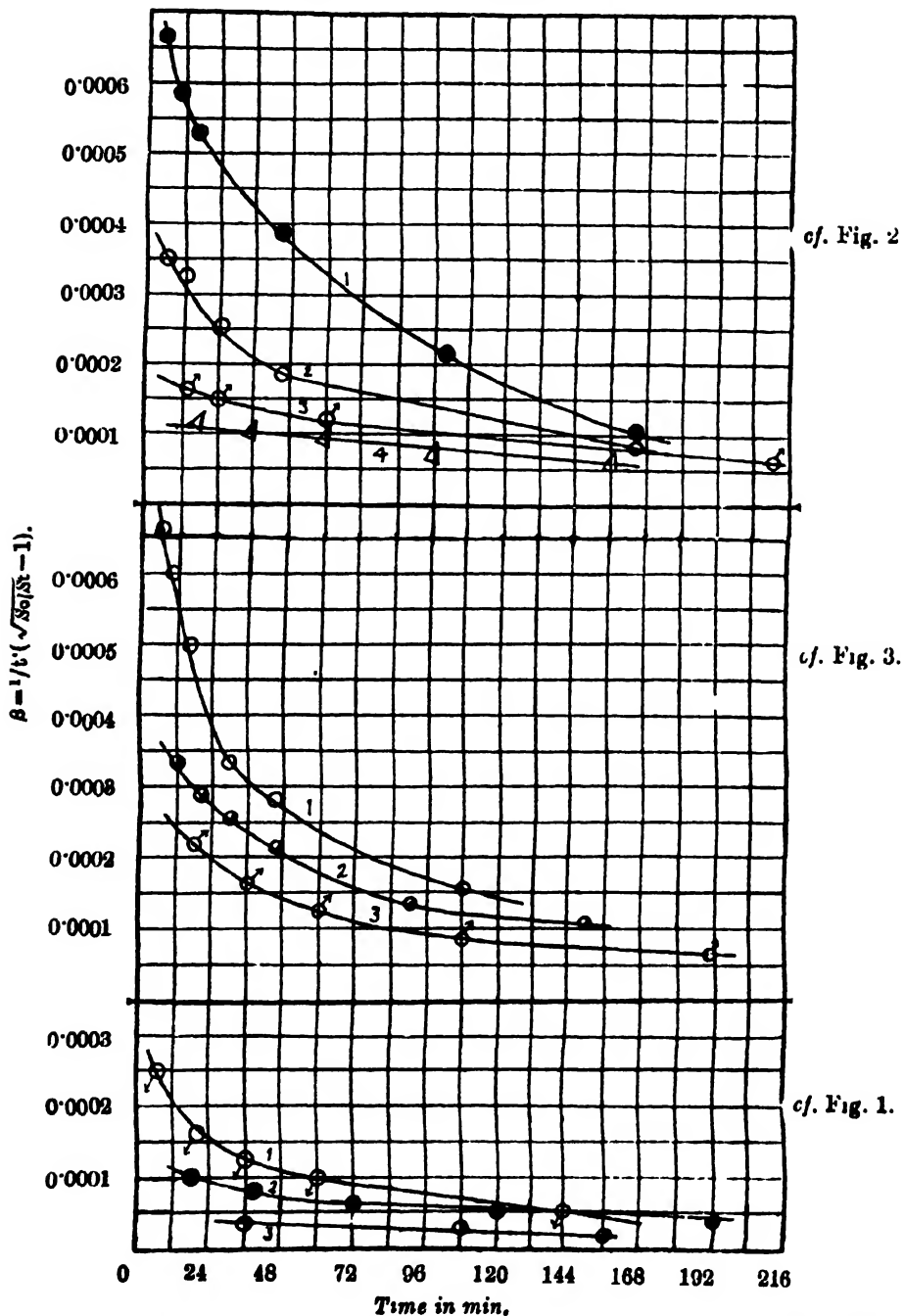
FIG. 4. Coagulation by  $\text{BaCl}_2$  (0.695 g.  $\text{MnO}_2$  per litre).FIG. 5. Coagulation by  $\text{KCl}$  (0.695 g.  $\text{MnO}_2$  per litre).

FIG. 6.  
Time variation of  $\beta$  in expts. Figs. 1—3.



Curves are marked and numbered similarly to the corresponding coagulation-time curves in Figs. 1—3.

It is known that in general and contrary to the requirements of Smolushowski's theory, the constant  $\beta$  diminishes with time in the



region of slow coagulation. Mukherjee and Mazumdar (*J. Chem. Soc.*, 1924, 126, 785) and others have tested the following equation deduced from Smoluchowski's theory.

$$\Sigma n_t = n_0 / (1 + \beta t) \quad \dots \quad \dots \quad \dots \quad \dots \quad (ii)$$

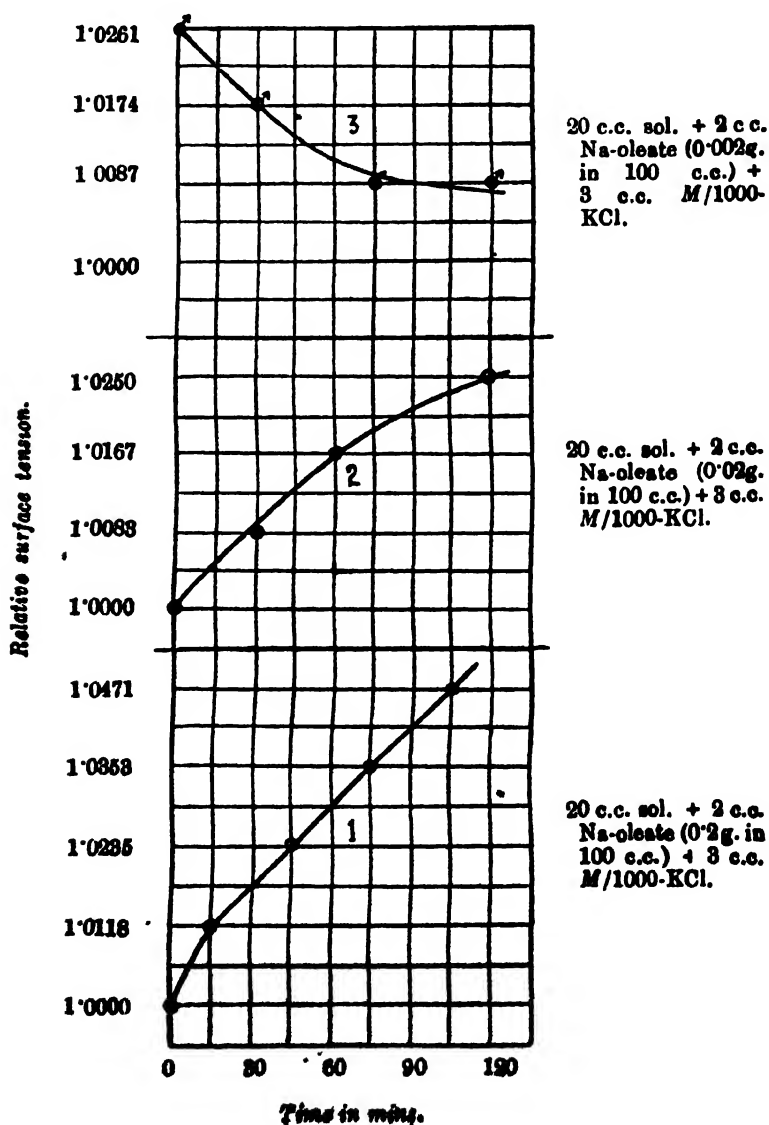
where  $\Sigma n_t$  denotes the total number of particles at a time during coagulation. It follows from this equation that starting with different samples of a given sol ( $n_0 = \text{constant}$ ) in coagulations due to different coagulators, the relative times  $t_1/T$ ,  $t_2/T$ ,  $t_3/T$ .....etc., corresponding to the same stage of coagulation, will be constant, that is, independent of the actual stage of coagulation, in the different series examined. A stage of coagulation is usually considered to be characterised by the value of some property such as the relative opacity etc., which has been found to vary continuously during the progress of coagulation. The last named and other workers have found that in slow coagulation  $t_1/T$  etc., is more constant, and that therefore the above theory is more followed, during the *initial* stages of coagulation than afterwards. This conclusion is contrary to the foregoing results showing the diminution of  $\beta$  during the different series of coagulation, calculated from equation (i). Essentially similar results were obtained previously (*cf.* Parts I—III, *loc. cit.*), the degree of coagulation being determined by a method different from that adopted in this work. It is interesting in this connection to examine Anderson's results on the *slow* coagulation of gold sols (*Trans. Faraday Soc.*, 1924, 19, 623);  $\beta$  was calculated from equation (i). These data show (Anderson does not however so state) that the diminution of  $\beta$  during slow coagulation is similar to what we have observed.

Equations (i) and (ii) being but deductions from the same theory, this contrariety between the two sets of results not noticed hitherto, is anomalous. This might, in a great measure, be due to the assumptions implied in estimating  $n_t$  and  $\Sigma n_t$  involved in equations (i) and (ii) respectively. It is important to emphasise here that especially in the case of polydisperse colloids, no method is available for measuring the degree of coagulation with the exception perhaps of the ultramicroscopic method. Deduction of the constancy of  $t_1/T$  from equation (ii) implies that a property like relative opacity is proportional to  $\Sigma n_{t_1}$ , or at least is a single valued function of  $\Sigma n_{t_1}$ . We have no means of examining the limits of the accuracy of this assumption. Likewise use of equation (i) necessitates some supposi-

tion in respect of  $n$ . We have assumed in calculating the foregoing results that  $n$  is proportional to the reciprocal of the surface tension of the coagulating sol. It might with equal justification be assumed that the last quantity is proportional to  $\Sigma n$ , since there is no *a priori* criterion in selecting any property as a quantitative index of the state of coagulation of a given sol. It is of interest therefore to

FIG. 7.

Coagulation by KCl in presence of sodium oleate.



examine the data (*cf.* Tables I—V) for  $t/T$  calculated on the last assumption, for the foregoing series of coagulations. It is seen from these results that in the majority of cases  $t/T$  is comparatively more constant during the early stages of coagulation than afterwards. It follows from these findings, therefore, that no deduction as regards the applicability of Smoluchowski's theory to a given region of coagulation is valid, unless we have more quantitative knowledge of the property used for following coagulation, as a function of  $n_1$  and  $\Sigma n_i$ . A fuller examination of this point will appear in a later communication.

One of the main difficulties in this work was that coagulation produced but small variation in the property used for following its course, *viz.*, surface tension. This together with the time of observation required in this method rendered the examination difficult especially of the initial stages in enough detail. It was thought therefore to increase the duration of the coagulation by introducing small amounts of a protector like sodium oleate, which would reduce the coagulation rate. It was found, however, that the relation between surface tension and the stage of coagulation is almost completely altered by but small changes in the concentration of the protector. Only three of the coagulation-time curves obtained in the course of these experiments have been given (Fig. 7) which serve to illustrate the effect just mentioned. In this connection it is of interest to mention the work of Anderson (*loc. cit.*) on the rapid coagulation of gold sols. Anderson added glycerol (which is a well known protector) to his sol in order to reduce the coagulation rate to a measurable value without changing the type of coagulation. In view of the results now discussed, it is obvious that the use of this artifice can only follow on testing whether the course of coagulation is materially disturbed by the addition of the protector.

TABLE I (*cf.* Fig. 1).

$T$	...	12'	24'	36'	60'	72	96'	132'
$t_1$	...	30'	58'	84'	120'	150'	198'	306'
$t_2$	...	66'	120'	180'	240'	300'	384'	540'
$t_1/T$	...	2.5	2.4	2.2	2.0	2.2	2.0	2.3
$t_2/T$	...	5.7	5.0	5.0	4.0	4.1	4.0	4.0

TABLE II (cf. Fig. 2)\*

$T$	...	4'	12'	36'	100'	180'
$t_1$	...	11'	32'	72'	168'	270'
$t_2$	• ..	22'	52'	96'	216'	372'
$t_1/T$	...	2.6	2.6	2.0	1.68	1.6
$t_2/T$	...	5.5	4.3	2.7	2.16	2.6

TABLE III (cf. Fig. 3).

$T$	...	6'	12'	24'	36'	40'	72'	84'
$t_1$	...	12'	30'	60'	76'	90'	146'	168'
$t_2$	...	24'	60'	108'	152'	180'	276'	300'
$t_1/T$	...	2.0	2.5	2.5	2.1	2.25	2.0	2.0
$t_2/T$	...	4.0	5.0	4.5	4.2	4.5	3.8	3.6

TABLE IV (cf. Fig. 4).

$T$	...	6'	12	15'	33'	60'	102'
$t_1$	...	24'	36'	51'	72'	120'	118'
$t_1/T$	...	4.0	4.0	3.4	2.1	2.0	1.1

TABLE V (cf. Fig. 5).

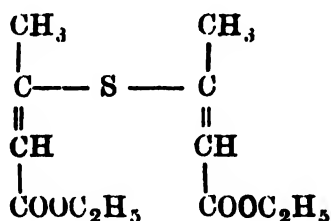
$T$	...	18'	36'	60'	90'	120''	150'
$t_1$	...	36'	60'	96'	135'	168'	216'
$t_1/T$	...	2.0	2.0	1.6	1.5	1.4	1.4

$T, t_1, t_2$ , etc. are times in minutes read off from curves in the corresponding Figures.

## Thioketonic Esters. Part II.

BY SUSIL KUMAR MITRA.

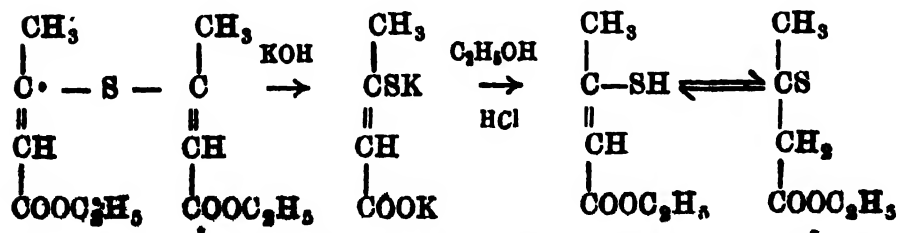
The method of the synthesis of thioketonic esters by the action of alcoholic potassium hydrosulphide on the corresponding unsaturated chloro ester is not satisfactory as the yield is small due to loss of  $\text{H}_2\text{S}$ . In the preparation of ethyl thioacetoacetate (*J. Indian Chem. Soc.*, 1931, 8, 471) by this method, the main product is a heavy oil boiling at  $155^\circ/15$  mm. The high boiling liquid is given the formula  $\text{C}_{12}\text{H}_{18}\text{O}_4\text{S}$  from its molecular weight determination and has probably the following constitution as suggested by considerations given below.



(1) It does not give any lead salt, gives no coloration with ferric chloride and does not decolourise alcoholic solution of iodine, hence the absence of a thiol group.

(2) Its inertness towards phenylhydrazine shows the absence of a thioketonic group.

(3) On treating it with alcoholic potash in the cold and acidifying a dark red oil is obtained which on esterification gives a considerable quantity of ethyl thioacetoacetate.



Pure ethyl thioacetoacetate on boiling with alcoholic hydrochloric acid or traces of piperidine is converted into this product with

evolution of sulphuretted 'hydrogen. This fact naturally suggests the formation of the compound in the method already described to be due to unreacted potassium hydrosulphide; the effect of which is most probably like piperidine on ethyl thioacetoacetate. The yield of ethyl thioacetoacetate is increased by adding alcoholic solution of potassium hydrosulphide (KSH absolutely free from KOH) over benzene solution of ethyl chlorocrotonate.

Thioketonic esters, *c.g.*, ethyl thioacetoacetate, ethyl thioacetone dicarboxylate have now been prepared in good yield without the formation of any by-product by passing  $H_2S$  into an alcoholic solution of the  $\beta$  ketonic esters, saturated with HCl gas. The reaction evidently takes place in the enol phase as otherwise polymerised products would result as suggested by Fromm and his collaborators (*Ber.*, 1889, 22, 2600; 1891, 24, 1457; *et seq.*). The thioketonic esters are purified by the decomposition of their lead salts in alcoholic suspension with  $H_2S$ .

Ethyl thiocetone dicarboxylate forms sodium derivative and the alkyl derivatives have been prepared by means of alkyl iodides in alcoholic sodium ethoxide diluted with benzene. The alkylated products are *S*-ethers; they do not form any lead salt; do not decolourise iodine nor give any coloration with ferric chloride and do not evolve  $H_2S$  on treatment with phenylhydrazine. The sodium derivative has evidently structure  $\begin{array}{c} | \\ C-SNa \\ || \end{array}$  and that C:S group can impart negative character to the methylene group in close proximity becomes conclusive.

#### EXPERIMENTAL.

- *Ethyl thioacetoacetate from ethyl chlorocrotonate.* (Modified method).—(A) An alcoholic solution of potassium hydrosulphide (24 g.), prepared by passing  $H_2S$  over balls of potassium in ether suspension, is added drop by drop into a benzene solution of ethyl chlorocrotonate (50 g.) at 48-50°, the solution being mechanically stirred. The benzene solution is washed with water and dehydrated. The oil obtained after removal of benzene, gives with freshly precipitated lead oxide yellow lead salt of ethyl thioacetoacetate. Pure ethyl thioacetoacetate is obtained by decomposing the lead salt in alcoholic suspension with  $H_2S$ , b. p. 75-80°/12 mm. Pyrazolone, m. p. 127°. Yield 50%.

*Ethyl  $\beta$ -thiodicrotonate* is obtained as a by-product in the preparation of ethylthioacetoacetate by means of alcoholic potassium hydrosulphide obtained either from caustic potash or from metallic potassium, even if the reaction is performed in benzene solution. The alcoholic wash of the lead salt is diluted with water and extracted with ether. The ethereal solution on dehydration is distilled in vacuum, when ethyl thiodicrotonate distils at  $155^{\circ}/15$  mm. (Found: C, 55.5 ; H, 7.2 ; S, 12.1 ; M. W., 254 (cryoscopic in benzene).  $C_{12}H_{18}O_4S$  requires C, 55.8 ; H, 6.9 ; S, 12.4 per cent; M. W., 258). The identical compound can also be obtained by boiling on water-bath an alcoholic solution of ethyl thioacetoacetate containing 1% HCl or trace of piperidine, till evolution of  $H_2S$  ceases. Yield 50%.

Ethyl thioacetoacetate can be obtained from this ester. The ester (50 g.) is dissolved in alcoholic potash (40 g. in 200 c.c.) in the cold and the red solution, on keeping for 2 days is acidified. The dark liquid, obtained after extraction with ether and dehydration over calcium chloride, is dissolved in alcohol (200 c.c.), the solution saturated with HCl at  $0^{\circ}$  and the ester formed is isolated in the usual manner. It is finally purified through lead salt and pure ethyl thioacetoacetate obtained in an yield of 10 g.

(B) *From ethyl acetoacetate*,  $H_2S$  gas is slowly passed into a solution of ethyl acetoacetate (100 g.) in alcohol (150 c.c.) saturated with HCl gas at  $0^{\circ}$ . On standing for 10 hours, crushed ice (2 lbs.) is poured into the solution, the ester extracted with ether, the ethereal solution washed with dilute sodium carbonate and the ether evaporated off. The rose-red oil is dissolved in rectified spirit and the solution added in thin stream over freshly precipitated lead oxide at  $0^{\circ}$  with vigorous stirring and the lead salt decomposed with  $H_2S$  in alcoholic suspension and the ester extracted with ether and distilled in vacuum at  $75-80^{\circ}/12$  mm, yield 85%. It forms with phenylhydrazine the pyrazolone (m.p.  $127^{\circ}$ ) described previously (*J. Indian Chem. Soc.*, 1931, 8, 471).

*Ethyl thioacetone dicarboxylate* is obtained by passing  $H_2S$  gas for 8 hours into an alcoholic solution of ethyl acetone dicarboxylate (50 g. in 100 c.c.), saturated with HCl. The solution is treated with ice, the ester extracted with benzene and the benzene layer washed with dilute sodium carbonate and the benzene removed under reduced pressure. It is finally purified by preparing the lead salt as in the previous case and decomposing it with  $H_2S$ . Yield 75%.

It is a rose-red sweet-smelling oil, decomposing at  $128^{\circ}/15$  mm. with evolution of  $H_2S$  producing an oil which does not contain sulphur. It decolourises iodine, produces green coloration with  $FeCl_3$  and evolves  $H_2S$  very energetically with phenylhydrazine. (Found: C, 49.4; H, 6.8; S, 14.5.  $C_9H_{14}O_4S$  requires C, 49.5; H, 6.4; S, 14.6 per cent).

*Propyl thioacetone dicarboxylic ethyl ester*.—Ethyl thioacetone dicarboxylate (10 g.) is dissolved in the cold in alcohol (30 c.c.) containing sodium (1 g.) and treated with propyl iodide (9 g.) and benzene (30 c.c.). The solution on keeping over night is heated on the water-bath for 4 hours. The oil which separates on adding water is extracted with benzene and the solution dehydrated and distilled in vacuum and the ester collected at  $220^{\circ}/30$  mm. (Found: C, 55.2; H, 8.3; S, 11.97.  $C_{12}H_{20}O_4S$  requires C, 55.3; H, 7.7; S, 12.3 per cent).

*Ethyl thioacetone dicarboxylic ethyl ester* is obtained by the interaction of ethyl bromide with ethyl thioacetone dicarboxylate as above. It boils at  $175^{\circ}/17$  mm. (Found: C, 53.3; H, 7.7; S, 12.7.  $C_{11}H_{18}O_4S$  requires C, 53.6; H, 7.3; S, 13.0 per cent).

The alkylated esters are colourless liquids possessing garlic odour. They are very stable and can be even boiled under atmospheric pressure with slight decomposition.

In conclusion I wish to convey my grateful thanks to Sir P. C. Rây for the kind interest he took in course of the investigation. Also I wish to express my indebtedness to Dr. P. B. Sircar for his valuable suggestion to estimate sulphur by the method of H. Ter Meulen (*Rec. Trav. Chim.*, 1922, 41, 112).



## Thioketonic Esters. Part III. Alkylation of Ethyl Thioacetoacetate.

BY PRAFULLA CHANDRA RÂY, SUSIL KUMAR MITRA  
AND NRIPENDRA NATH GHOSH.

Ethyl thioacetoacetate was suitably alkylated by the action of alkyl halides on its sodium derivative obtained by the action of the ester over metallic sodium in benzene suspension. The following derivatives were prepared by the action of the corresponding halides on the sodium derivative of ethyl thioacetoacetate :

Ethyl  $\beta$ -ethylmercaptocrotonate (b.p.  $114-17^{\circ}/15$  mm.)

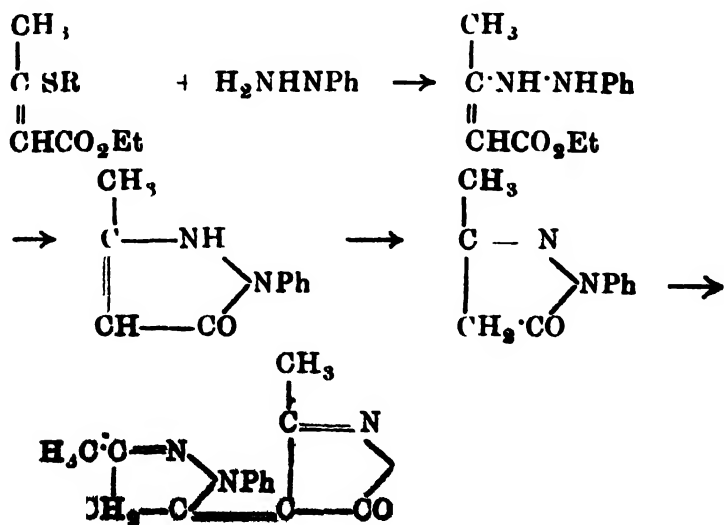
Ethyl  $\beta$ -*n*-propylmercaptocrotonate (b.p.  $117-20^{\circ}/15$  mm.)

Ethyl  $\beta$ -*n*-amylmercaptocrotonate ( $126-28^{\circ}/15$  mm.)

Ethyl  $\beta$ -benzylmercaptocrotonate (m.p. 68, b.p.  $155-60^{\circ}/15$  mm.)

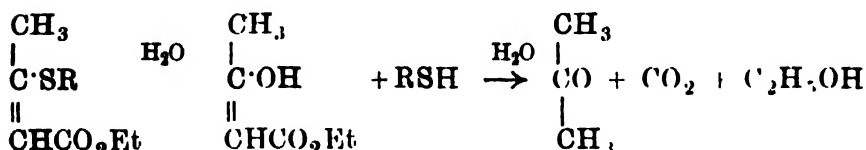
Ethyl  $\beta$ -(benzoylmethyl)-mercaptocrotonate (m.p.  $85^{\circ}$ ).

On treatment with phenylhydrazine, these compounds do not give sulphuretted hydrogen under ordinary conditions, thus showing the absence of a free thioketonic group in them. On treatment with phenylhydrazine at its boiling point, however, they evolve mercaptans and a considerable quantity of dehydropyrazolone is obtained. The reaction can evidently be represented as follows :—



This constitution of the ethers was further supported by the fact that it decolourised bromine water. They did not give any lead salt thus showing the absence of a free thiol group in them. In the formation of *S*-ethers, ethyl thioacetoacetate differs from ethyl acetoacetate which forms mainly *C*-derivatives under ordinary conditions. The action of reducing agents gave rise to mercaptans, thus showing that the alkyl groups are linked to the sulphur atom.

On boiling these compounds with dilute acids, the degradation products were found to be acetone and the corresponding mercaptans. The reaction seems to take place as follows:—



The behaviour of ethyl  $\beta$ -thiodicrotonate towards alcoholic potash (cf. *J. Indian Chem. Soc.*, 1933, 10, 71) in conjunction with the results obtained by boiling the alkylated products with dilute acids leads us to conclude that although these alkyl derivatives of the esters are similar in structure to alkyl sulphide, they differ from the latter in being more sensitive to chemical reagents than the alkyl sulphides. Evidently the sulphur atom is under some influence to which this increased labile nature can be attributed.

These alkyl derivatives are found to distil under reduced pressure through a long range of temperature, but analytical data of the lowest and the highest boiling fractions were found to be identical. This may be ascribed to the presence of geometrical isomers of the products. This inference was found to be correct on an examination of the acid obtained by careful hydrolysis of the ethyl derivative by means of alcoholic potash. This acid was found to melt at 86° whereas its *cis*- and *trans*-forms, (obtained by the action of the sodium salt of ethyl mercaptans on *cis*- and *trans*-chlorocrotonic acids (*Annalen*, 1889, 254, 284; *Ber.*, 1899, 32, 2806) melt at 112° and 92° respectively. The acid was probably a mixture of these two isomers.

The following acids were obtained under identical conditions: (1)  $\beta$ -Ethylmercaptocrotonic acid (m.p.  $85^\circ$ ). (2)  $\beta$ -*n*-Propylmercaptocrotonic acid (m.p.  $70^\circ$ ). (3)  $\beta$ -Benzylmercaptocrotonic acid (m.p.  $184^\circ$ ).

The free acid from ethyl  $\beta$ -thiodicrotonate could not be isolated under similar conditions (cf. *J. Indian Chem. Soc.*, 1938, 10, 71. This compound is evidently more sensitive to part with sulphur than the alkyl derivatives mentioned above.

#### EXPERIMENTAL.

**Ethyl  $\beta$ -ethylmercaptocrotonate.**—Ethyl thioacetoacetate (30 g.), diluted with benzene, was treated with metallic sodium (5 g.) in benzene suspension. During the treatment (3 hours) the reaction flask was cooled in ice-water with constant shaking and the whole was kept for 2 hours. Ethyl iodide (34 g.) was added to sodium derivative of the ester and the whole was refluxed on a water-bath for 7 hours. The product was then extracted with benzene; the extract after drying over calcium chloride was made free from benzene and subjected to vacuum distillation. The fractions between (i)  $72^\circ$ - $73^\circ$  (ii)  $75^\circ$ - $114^\circ$  and (iii)  $114^\circ$ - $117^\circ$  under 15 mm. pressure were collected [Found: (i) C, 55.02; H, 8.57; S 18; (iii) C, 55.0; H, 8.1; S, 18.02; M.W., 170.2.  $C_8H_{14}O_2S$  requires C, 56.1; H, 8.1; S, 18.36 per cent; M.W., 174)

**Ethyl  $\beta$ -*n*-propylmercaptocrotonate**—Ethyl thioacetoacetate (30g.) was treated with sodium (5 g.) as before and the sodium derivative was then refluxed with *n*-propyl iodide (38 g.) on a water-bath for 7 hours. The product was then isolated as in the previous case and distilled in vacuum. The fraction between  $117^\circ$ - $120^\circ$ /15 mm. was collected. (Found: C, 56.7; H, 9.4; S, 16.71; M.W., 189.9.  $C_9H_{16}O_2S$  requires C, 57.4; H, 9.0; S, 17.0 per cent; M.W., 188).

**Ethyl  $\beta$ -*n*-amylmercaptocrotonate.**—Ethyl thioacetoacetate (30g.) was treated with sodium (5g.) as before and the product was refluxed with *n*-amyl iodide on a water-bath for 7 hours. On distillation under 15 mm. pressure, the fraction between  $126$ - $28^\circ$  was collected. (Found: S, 14.58.  $C_{11}H_{20}O_2S$  requires S, 14.82 per cent).

**Ethyl  $\beta$ -benzylmercaptocrotonate.**—The sodium derivative obtained from ethyl thioacetoacetate (30g.) and sodium (5g.) was refluxed with

benzyl chloride (34g.) on a water-bath for 12 hours. The product was isolated as usual and distilled under 15 mm. pressure. The fraction between 155°-160° was collected and found to solidify after 2 or 3 days, m.p. 68°. (Found: S, 13.45.  $C_{13}H_{16}O_2S$  requires S, 13.56 per cent).

*Ethyl  $\beta$ -(benzoylmethyl)-mercaptocrotonate.*—The sodium derivative prepared as before was refluxed with benzene solution of *o*-bromoacetophenone (41g.) on a water-bath for 12 hours. The impure liquid product was solidified with freezing mixture and the solid product was isolated by rapid filtration and finally crystallised from ethyl alcohol, m.p. 85°. (Found: S, 12.06.  $C_{14}H_{16}O_3S$  requires S, 12.13 per cent).

*General properties of the alkylated products.*—The alkylated products do neither form lead salts nor give any coloration with ferric chloride. With phenylhydrazine, they give no reaction at the ordinary temperature; but on heating the mixture on sand-bath, the mercaptans are given off which can be detected with lead acetate paper and from the reaction mixture, a considerable quantity of dehydropyrazolone is obtained. They decolourise bromine water immediately and have no constant boiling point. When they are subjected to reducing action, the mercaptans are given off, and on boiling with dilute mineral acids the mercaptans with carbon dioxide are evolved. They can generally be hydrolysed with alcoholic potash at the ordinary temperature to the corresponding  $\beta$ -alkylmercaptocrotonic acids.

#### *Action of Phenylhydrazine on Alkylated Products*

*On n-propyl derivative.*—Ethyl  $\beta$ -n-propylmercaptocrotonate (3g) was heated with phenylhydrazine (3g.) on sand-bath with an air-condenser for a few hours. When tested with lead acetate paper, a mercaptan was found to evolve, frequently accompanied by  $H_2S$  gas, due perhaps to the decomposition of mercaptan at high temperatures. After completion of the reaction, the products were washed with ether and crystallised from pyridine, m.p. 380° (decomp.). (Found: N, 16.89. dehydropyrazolone requires N, 17.0 per cent).

*On benzyl derivative.*—Equimolecular quantities of ethyl  $\beta$ -benzylmercaptocrotonate and phenylhydrazine were heated on sand-bath, when  $H_2S$  gas was evolved. On completion of the reaction, the residue gave out smell similar to that of dibenzyl sulphide and it was then washed with acetone. A product was obtained melting at 380° (decomp.) (dehydropyrazolone, m.p. 380°).

*Action of dilute mineral acids on ethyl  $\beta$ -ethylmercaptocrotonate.*—Ethyl  $\beta$ -ethylmercaptocrotonate (15g.) was heated with 10%  $\text{H}_2\text{SO}_4$  (100 c.c.) on wire gauze under reflux. The escaping gases were passed successively through ethyl alcohol and a solution of barium hydroxide. The heating was continued till carbon dioxide ceased to evolve. Acetone was detected in the aqueous solution by the usual colour reactions.

The alcohol, over which the escaping gases were passed, was treated with alcoholic solution of iodine till the colour of iodine did not vanish. The resulting product was extracted with ether and washed with sodium thiosulphate solution to remove excess of iodine. After evaporating off the ether, it boiled at  $152^\circ$  and was found to be diethyl disulphide (b. p.  $152^\circ$ ).

*Action of Alcoholic Potash on Alkylated Products.*

*$\beta$ -Ethylmercaptocrotonic acid.*—Ethyl  $\beta$ -ethylmercaptocrotonate (1 mol.) was kept with 12% alcoholic potash (1 mol.) over night. The mixture was then diluted with ice water and acidified with dilute hydrochloric acid. The precipitated product was filtered and crystallised from methyl alcohol and the crystals were washed with petroleum ether, m. p.  $86^\circ$ . (Found S, 21.46.  $\text{C}_6\text{H}_{10}\text{O}_2\text{S}$  requires S, 21.92 per cent).

*$\beta$ -n-Propylmercaptocrotonic acid.*—Ethyl  $\beta$ -n-propylmercaptocrotonate (1 mol.) was treated as above with one mol. of alcoholic potash. The solid product was crystallised from methyl alcohol and washed with petroleum ether, m. p.  $70^\circ$ . (Found S, 19.74.  $\text{C}_7\text{H}_{12}\text{O}_2\text{S}$  requires S, 20.0 per cent).

*$\beta$ -Benzylmercaptocrotonic acid.*—Ethyl  $\beta$ -benzylmercaptocrotonate was treated as before with alcoholic potash. The acid obtained was crystallised from ethyl alcohol and the crystals were washed with petroleum ether, m. p.  $134^\circ$ . (Found: S, 15.54.  $\text{C}_{11}\text{H}_{12}\text{O}_2\text{S}$  requires S, 15.88 per cent).

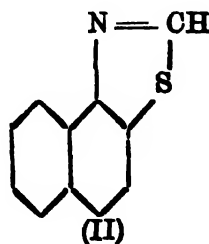
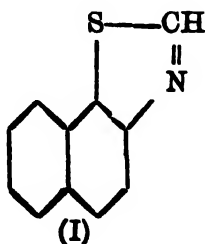
*Reduction of ethyl  $\beta$ -ethylmercaptocrotonate.*—Ethyl  $\beta$ -ethylmercaptocrotonate (15g.) was subjected to the reducing action of zinc-amalgam and dilute hydrochloric acid and kept over-night. A mercaptan was found to evolve when tested with lead acetate paper. On completion of the reaction, the product was extracted with ether. The product was found to contain no sulphur and had boiling point  $92^\circ$ ; it was probably ethyl propionate (b. p.  $98^\circ$ ).



# **Studies in the Naphthathiazole Series. Part I. The Constitution of the Bromo-addition Compounds of Bromo-substituted Alkylamino- $\beta$ -naphthathiazoles Obtained in the Bromination of $s$ - $\alpha$ -Naphthylalkyl thiocarbamides.**

BY CHIRAG HASAN AND ROBERT FERGUS HUNTER.

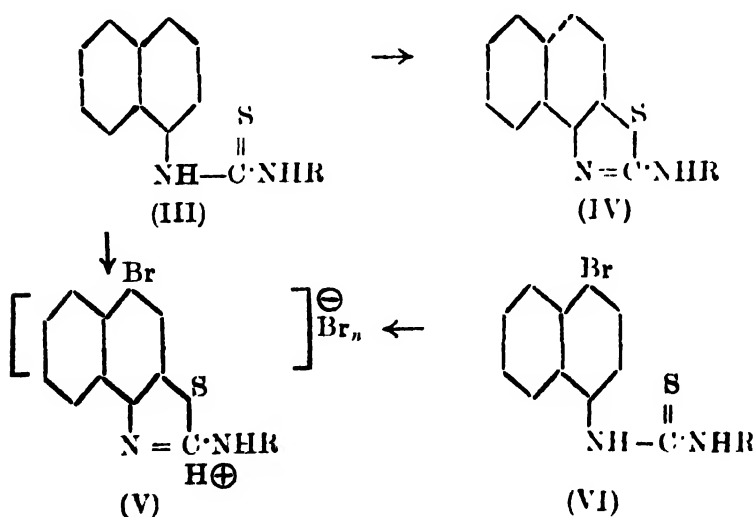
In view of the manner in which the different syntheses of benzthiazole derivatives have been exploited by chemical investigators to both academic and technical ends, it appears curious that the study of the naphthalene homologues of these compounds has previously attracted comparatively little attention. Derivatives of  $\alpha$ - and  $\beta$ -naphthathiazoles (I and II respectively) were first obtained by Hofmann in 1887 by the thionation of certain naphthalides (*Ber.*, 1887, 20, 1798), and in the same year, Jacobson prepared 2-methyl- $\beta$ -naphthathiazole by oxidation of an alkaline solution of thioacet- $\alpha$ -naphthalide with potassium ferricyanide (*ibid.*, p. 1895). In the following year, the isomeric methyl- $\alpha$ -naphthathiazole was synthesised by the same reaction (Jacobson and Sullwald, *Ber.*, 1888, 21, 2624), and the 1-thiol- $\alpha$ - and 2-thiol- $\beta$ -naphthathiazoles were subsequently prepared by Jacobson and Frankenbacher three years later (*Ber.*, 1891, 24, 1400) by heating the corresponding naphthylthiocarbimides with sulphur.



With the exception of the synthesis of certain aminonaphthathiazole derivatives (Hunter, *J. Chem. Soc.*, 1925, 127, 2270 ; 1926, 1885, and later)\* and the investigation of the cyanine dyes derived from quaternary salts of the methylnaphthathiazoles (Hamer, *J. Chem. Soc.*, 1929, 2598), however, there has been little develop-

ment in the chemistry of the naphthathiazole group in the last forty years. The object of the present series of papers is therefore to study the unsaturation and tautomeric mobility of heterocyclic compounds of naphthathiazole derivatives, on lines similar to those which are being followed in the investigation of benzthiazole derivatives (Hunter, *J. Chem. Soc.*, 1930, 125; Hunter and Jones, *ibid.*, p. 2190; Dyson, Hunter, Jones and Styles, *J. Indian Chem. Soc.*, 1931, 8, 147).

In an earlier investigation it was observed that the interaction of an equimolecular proportion of bromine with a solution of a *s*- $\alpha$ -naphthylalkylthiocarbamide (III) in chloroform gives rise to a hydrobromide of the corresponding 2-alkylamino  $\beta$ -naphthathiazole (IV) (Dyson, Hunter and Morris, *J. Chem. Soc.*, 1932, 2282), whereas bromination under the usual conditions of thiazole cyclisation (Hunter, *J. Chem. Soc.*, 1925, 127, 2023, and later) leads to the production of bromo-addition compounds of bromo-substitution derivatives. These bromo-addition compounds have now been shown to be *hydroperbromides* of the corresponding 8-bromo-2-alkylamino- $\beta$ -naphthathiazoles (V) by their preparation from the corresponding *s*-4-bromo- $\alpha$ -naphthylalkylthiocarbamides (VI), which were synthesised from 4-bromo- $\alpha$ -naphthylthiocarbimide obtained from 4-bromo- $\alpha$ -naphthylamine and thiocarbonyl chloride in the usual way (Dyson, George and Hunter, *J. Chem. Soc.*, 1926, 3041; 1927, 436).



The bromination of *s*- $\alpha$ -naphthylmethylthiocarbamide in the presence of a large excess of the halogen gives rise to a highly



unstable *hydropentabromide* of 8-bromo-2-methylamino- $\beta$ -naphthathiazole (V, R=Me ;  $n=5$ ),\* which is also obtained from the 4-bromonaphthylmethylthiocarbamide (VI, R=Me), under similar conditions. Bromination in the presence of a lower concentration of bromine gives rise to a *hydrotribromide* of the bromomethylamino-naphthathiazole (V, R=Me ;  $n=3$ ), which can also be prepared by degradation of the *hydropentabromide* in a vacuum over potassium hydroxide, and by bromination of *s*-4-bromo- $\alpha$ -naphthylmethylthiocarbamide in the presence of a concentration of the halogen lower than that required for the production of the unstable *hydropentabromide*. As might be anticipated, this *hydrotribromide* regenerates the *hydropentabromide* on bromination in chloroform.

On bromination in chloroform in the presence of a concentration of bromine still lower than that required for the production of the *hydrotribromide*, *s*- $\alpha$ -naphthylmethylthiocarbamide yielded a yellow-orange *hydrodibromide* of the 8-bromomethylaminonaphthathiazole base, which was also obtained by degradation of the *hydrotribromide* in a desiccator containing potassium hydroxide. This substance, which was the most stable of the three bromo-addition compounds under ordinary laboratory conditions, is evidently analogous to the *hydrodibromide* of 1-amino-benzthiazole (Hunter, *J. Chem. Soc.*, 1930 125) and probably con-

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tains a  $\text{Br}_2$  ion, whose formulation involves the operation of a lone singlet linkage (cf. Hunter, *Chem. and Ind.*, 1932, 51, 939).

*s*- $\alpha$ -Naphthylethylthiocarbamide behaved similarly to the methylthiocarbamide and gave rise to a *hydropentabromide*, a *hydrotribromide*, or a *hydrodibromide* of 8-bromo-2-ethylamino- $\beta$ -naphthathia-

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This formulation is not necessarily meant to imply the existence of a  $\text{Br}_2$  ion in highly unstable compounds of this type. The bromine which is so readily eliminated from the *hydropentabromide* of 8-bromo-2-methylamino- $\beta$ -naphthathiazole with the production of the more stable *hydrotribromide*, for instance, may possibly be present in the form of a physical mixture, the solid phase of which has the

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composition, [Base, H]  $\text{Br}_3$ ,  $\text{Br}_2$  (cf. Dyson, Hunter, Jones and Styles, *loc. cit.*). The seat of the phenomenon of polybromide formation of this type is, however, the bromine ion of the *hydrobromide* of the base produced by thiazole cyclisation (Hunter, *J. Indian Chem. Soc.*, 1932, 9, 435), and it is reasonable to assume that the affinity which leads to the production of a *hydrotribromide* complex will be

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relayed, in some measure at least, through the bromine atoms of the  $\text{Br}_2$  ion.

zole, according to the conditions of the reaction. The hydrotribromide was also obtained from the hydropentabromide by loss of bromine as in the case of the methyl derivative. The constitution of these bromo-addition compounds was established by synthesis from *s*-4-bromo- $\alpha$ -naphthylethylthiocarbamide as in the previous case.

The bromination of *s*- $\alpha$ -naphthyl-*iso*-amylthiocarbamide was also re-examined, and it was observed that this thiocarbamide gave rise to a *hydropentabromide* or a *hydrodibromide* of the 8-bromo-2-*iso*-amylamino base, according to the conditions of the experiment. This hydropentabromide was also prepared from the 4-bromo- $\alpha$ -naphthyl-*iso*-amylthiocarbamide by treatment with a considerable excess of the halogen, and yielded the hydrotribromide by loss of a molecule of bromine as in the case of the methyl and ethyl compounds.

#### EXPERIMENTAL.

The *s*- $\alpha$ -naphthylalkylthiocarbamides are much more conveniently prepared by condensation of  $\alpha$ -naphthylthiocarbimide and the corresponding alkylamine than by condensation of  $\alpha$ -naphthylamine with the requisite alkylthiocarbimides (Dyson and Hunter, *Rec. trav. chim.*, 1926, **45**, 421; Dyson, Hunter and Soyka, *J. Chem. Soc.*, 1926, **129**, 2964). Considerable difficulty was experienced in preparing  $\alpha$ -naphthylthiocarbimide by the methods given in the literature. It was most readily obtained from *s*-di- $\alpha$ -naphthylthiocarbamide and boiling acetic anhydride by the method used for the preparation of the  $\beta$ -isomer (Hunter and Jones, *J. Chem. Soc.*, 1930, 912), but the yield was always poor (10 to 20 per cent). The thiocarbimide was also prepared by adding  $\alpha$ -naphthylamine (1 mol.) in chloroform (5 vols.) to a well-stirred suspension of thiocarbonyl chloride (1.3 mols.) in water (10 vols.) at laboratory temperature; stirring being continued for a further 30 minutes after the completion of the addition of the amine solution, and the thiocarbimide isolated in the usual way (Dyson, George and Hunter, *loc. cit.*).

**8-Bromo-2-methylamino- $\beta$ -naphthathiazole hydropentabromide** (V, R=Me;  $n=5$ ).—(i) *Bromination of s*- $\alpha$ -Naphthylmethylthiocarbamide. A solution of the naphthylmethylthiocarbamide (m.p. 198°) in chloroform (0.2 g. in 4 c.c.) was treated with bromine (0.8 c.c. in 0.7 c.c. of the same solvent) and the mixture was heated under reflux on a water-bath for 5 minutes. The hydropentabromide finally separated in orange-red rhombic crystals which were transferred to

porous earthenware, placed in a vacuum desiccator which was rapidly exhausted on an oil pump, and the crystals analysed with the usual precautions (Dyson, Hunter and Soyka, *J. Chem. Soc.*, 1929, 468) after one or two minutes. [Found: Br (total), 70.0; Br (labile), 45.8.  $C_{12}H_9N_2BrS$ ,  $HBr(Br_4)$  requires Br (total), 69.1; Br (labile), 46.1 per cent]. Just after the moment of its isolation the bromo-addition compound had m. p.  $135^\circ$  (decomp.), but this rose to  $163^\circ$  (decomp.), which is the m.p. of the hydrotribomide, after a lapse of 10 minutes (Dyson, Hunter and Soyka, *J. Chem. Soc.*, 1926, 2964, recorded this for the m.p. of the supposed "hexabromide of 2 methyl-amino- $\beta$ -naphthathiazole"). On reduction with sulphurous acid and sulphur dioxide, and basification with ammonia ( $d\ 0.880$ ), the hydro-pentabromide yielded 8-bromo-2-methylamino- $\beta$ -naphthathiazole, which crystallised from alcohol-ethyl acetate (animal charcoal) in aggregates of small needles, m.p.  $194-95^\circ$ , identical with the specimen synthesised from 4-bromo- $\alpha$ -naphthylthiocarbimide by way of *s*-4-bromo- $\alpha$ -naphthylmethylthiocarbamide. (Found: Br, 27.2,  $C_{12}H_9N_2BrS$  requires Br, 27.3 per cent). The *acetyl* derivative, obtained by boiling a solution of 8-bromo-2-methylamino- $\beta$ -naphthathiazole in acetic anhydride for a few minutes and diluting the solution with alcohol, separated from alcohol in microscopic needles, m.p.  $208^\circ$ . (Found: Br, 24.2.  $C_{14}H_{11}ON_2BrS$  requires Br, 23.8 per cent).

(ii) *Synthesis from 4-Bromo- $\alpha$ -naphthylthiocarbimide by way of s-4-Bromo- $\alpha$ -naphthylmethylthiocarbamide.* 4-Bromo- $\alpha$ -naphthylthiocarbimide.—A solution of 4-bromo- $\alpha$ -naphthylamine (9 g.) in chloroform (60 c.c.) was gradually added to a mechanically stirred suspension of thiocarbonyl chloride (9 c.c.) in water (60 c.c.) in the course of 20 minutes, and vigorous stirring was continued for a further 10 minutes. The sticky product was separated and kept overnight in a desiccator containing sulphuric acid and extracted with boiling benzene in which the dibromo-dinaphthyl-thiocarbamide which was formed as a by-product was practically insoluble. The *thiocarbimide* crystallised from this solvent in small thick needles, m.p.  $90^\circ$ . (Found: Br, 30.0.  $C_{11}H_6NBrS$  requires Br, 30.3 per cent) *s*-4-Bromo- $\alpha$ -naphthylmethylthiocarbamide. A suspension of the naphthylthiocarbimide (1 g.) in alcohol (10 c.c.) was treated with a 33 per cent solution of methylamine (1.6 c.c.), when the thiocarbimide dissolved on warming, giving a dark brown solution which was concentrated. The crystals of the methylthiocarbamide thus obtained

were washed with methyl alcohol to remove the coloured impurity, and had m.p.  $179^{\circ}$ . (Found: Br, 27.0.  $C_{12}H_{11}N_2BrS$  requires Br, 27.1 per cent). A solution of the bromonaphthylmethylthiocarbamide (0.2 g.) in chloroform (5 c.c.) was treated with bromine (0.6 c.c. in 1 c.c. of the same solvent) and the mixture was heated on a water bath under reflux for 5 minutes. The hydropentabromide obtained in this way had m.p.  $186^{\circ}$  after rapid drying in vacuum. [Found: Br (total), 70.1; Br (labile), 46.0 per cent], and yielded 8-bromo-2-methylamino- $\beta$ -naphthathiazole on reduction, which had m.p.  $194^{\circ}$  alone, and when mixed with the specimen already described.

*8-Bromo-2-methylamino- $\beta$ -naphthathiazole hydrotribromide* (V, R=Me;  $n=3$ ).—(i) *Bromination of s- $\alpha$ -Naphthylmethylthiocarbamide*. The naphthylmethylthiocarbamide (0.2 g.) in chloroform (4 c.c.) was treated with bromine (0.6 c.c. in 0.6 c.c. of chloroform) and the mixture was heated on a water bath for 5 minutes. A yellow precipitate first separated which acquired a pinkish colour, which was dried on porous earthenware in a vacuum. The *hydrotribromide* formed pink needles, m.p.  $162-64^{\circ}$  (decomp. blackening at  $115-125^{\circ}$ ). [Found: Br (total), 60.0; Br (labile), 29.1.  $C_{12}H_9N_2BrS$ , HBr ( $Br_2$ ) requires Br (total), 60.0; Br (labile), 30.0 per cent].

(ii) *Degradation of the hydropentabromide of 8-Bromo-2-methylamino- $\beta$ -naphthathiazole*. The hydropentabromide of the 8-bromo-naphthathiazole was kept in a vacuum over potassium hydroxide, when the red crystals decomposed with loss of bromine yielding crystals of the hydrotribromide m.p.  $162.163^{\circ}$ . [Found: Br (total), 61.4; Br (labile), 29.9 per cent].

(iii) *Preparation from s-4-Bromo- $\alpha$ -naphthylmethylthiocarbamide and Bromine*. A solution of the bromonaphthylthiocarbamide in chloroform (0.2 g. in 5 c.c.) was treated with bromine (0.4 c.c. in 0.7 c.c. of the same solvent), and the mixture was heated for 5 minutes under reflux when the hydrotribromide was obtained, m.p.  $163^{\circ}$ . [Found: Br (total), 60.9; Br (labile), 30.0 per cent]. Bromination of the hydrotribromide in chloroform solution yielded the hydropentabromide of 8-bromo-2-methylamino- $\beta$ -naphthathiazole which was identified by its appearance, m.p. and analysis [Found: Br (total), 69.8; Br (labile), 46.0 per cent].

*8-Bromo-2-methylamino- $\beta$ -naphthathiazole hydridibromide*.—A solution of s- $\alpha$ -naphthylmethylthiocarbamide (0.6 g.) in chloroform (20 c.c.) was treated with bromine (1.2 c.c.) and the mixture was

heated for 5 minutes, when the *hydroadibromide* was obtained in the form of fine orange yellow needles, m.p. 195° (decomp.). [Found: Br (total), 52.9; Br (labile), 17.6.  $C_{12}H_9N_2BrS$ ,  $HBr(Br)$  requires Br (total), 52.9; Br (labile), 17.6 per cent]. This compound was the most stable of these three bromo-addition compounds and was also obtained by keeping the hydrotribromide in a desiccator over potassium hydroxide for 4 days. The specimen obtained in this way, had m.p. 197°. [Found: Br (total), 52.4; Br (labile), 17.4 per cent].

*8-Bromo-2-ethylamino-β-naphthathiazole* *hydropentabromide* (V, R = Et; n = 5) (i) *Bromination of s-α-Naphthylethylthiocarbamide*. A solution of *s-α-naphthylethylthiocarbamide* (m.p. 124°) in chloroform (0.2 g. in 4 c.c.) was treated with bromine (0.6 c.c. in 0.8 c.c. of chloroform) and the mixture was heated for 6 minutes on a water bath under reflux, and then concentrated under reduced pressure at laboratory temperature. The orange-red *hydropentabromide* was obtained, m.p. 93°. [Found: Br (total), 67.8; Br (labile), 45.0.  $C_{13}H_{11}N_2BrS$ ,  $HBr(Br_4)$  requires Br (total), 67.7; Br (labile), 45.2 per cent]. On reduction with sulphurous acid and sulphur dioxide it yielded *8-bromo-2-ethylamino-β-naphthathiazole* which crystallised from alcohol-ethyl acetate in soft silky needles, m.p. 147°. (Found: Br, 10.0.  $C_{13}H_{11}N_2BrS$  requires Br, 10.1 per cent). The *acetyl* derivative, prepared by heating a solution of the base in acetic anhydride for a few minutes and diluting with alcohol, crystallised in colourless prisms, m.p. 172-73°. (Found: S, 9.2.  $C_{15}H_{13}ON_2BrS$  requires S, 8.8 per cent).

(ii) *Synthesis from s-4-Bromo-α-naphthylethylthiocarbamide*. *s-4-Bromo-α-naphthylethylthiocarbamide*. The gum obtained by concentrating a mixture of 4-bromo- $\bar{\alpha}$ -naphthylthiocarbimide (1g.) in alcohol (10 c.c.) and ethylamine (1.6 c.c. of a 33 per cent solution in water) was kept overnight, and then triturated with ether, when it solidified. The ethylthiocarbamide could not, however, be obtained crystalline and had m.p. 82° after being washed free from gummy impurities by ether. (Found: Br, 25.0.  $C_{13}H_{13}N_2BrS$  requires Br, 25.8 per cent). A solution of this product in chloroform (0.2 g. in 4 c.c.) was treated with bromine (0.8 c.c. in 0.5 c.c. of chloroform) and the mixture was concentrated in a vacuum after being heated under reflux for 5 minutes. The crystals of the *hydropentabromide* obtained in this way were brown coloured, due evidently to an impurity in the bromonaphthylethylthiocarbamide, but had similar properties to those of the specimen already described,

m.p. 94°. [Found: Br (total), 67·7; Br (labile), 45·1 per cent]. On reduction with sulphurous acid, it yielded 8-bromo-2-ethylamino- $\beta$ -naphthathiazole, which was undepressed by admixture with the specimen already described.

**8-Bromo-2-ethylamino- $\beta$ -naphthathiazole hydrotribromide.** (i) *Bromination of s- $\alpha$ -Naphthylethylthiocarbamide.* A solution of the naphthylethylthiocarbamide in chloroform (0·2 g. in 4 c.c.) was treated with bromine (0·6 c.c. in 0·8 c.c. of chloroform) and the mixture was heated on a water bath for 6 minutes when the *hydrotribromide* separated in yellow crystals, m.p. 204°. [Found: Br (total), 58·2; Br (labile), 29·0.  $C_{13}H_{11}N_2BrS$ ,  $HBr(Br_2)$  requires Br (total), 58·0; Br (labile), 29·1 per cent].

(ii) *Degradation of 8-Bromo-2-ethylamino- $\beta$ -naphthathiazole hydropentabromide.* The hydrotribromide was also obtained by keeping the hydropentabromide in a desiccator over potassium hydroxide; the specimen obtained in this way had m.p. 203°. [Found: Br (total), 58·8; Br (labile), 29·0 per cent].

(iii) *Synthesis from s-4-Bromo- $\alpha$ -naphthylethylthiocarbamide.* The hydrotribromide of 8-bromo-2-ethylamino- $\beta$ -naphthathiazole was also prepared as in the case of the methyl derivative by treating a solution of the bromonaphthylethylthiocarbamide (0·2 g.) in chloroform (4 c.c.) with bromine (0·7 c.c. in 0·7 c.c. of chloroform) in the usual way and identified by m.p. and analysis. [Found: Br (labile), 29·0 per cent.]. On reduction with sulphurous acid and sulphur dioxide, it yielded 8-bromo-2-ethylamino- $\beta$ -naphthathiazole as in the case of the higher bromo-addition compound.

**8-Bromo-2-isoamylamino- $\beta$ -naphthathiazole hydropentabromide (V, R = iso- $C_5H_{11}$ ; n = 5).** (i) *Bromination of s- $\alpha$ -Naphthylisoamylthiocarbamide.* A solution of the isoamylthiocarbamide in chloroform (0·2 g. in 4 c.c.) was treated with bromine (0·8 c.c. in 0·6 c.c. of chloroform) and the mixture was heated for 5 minutes, and the solution concentrated under reduced pressure at laboratory temperature. The *hydropentabromide* formed orange red unstable crystals which were rapidly dried on porous earthenware in vacuum and analysed; m.p. 79-80°. [Found: Br (total), 64·1; Br (labile), 42·6.  $C_{16}H_{17}N_2BrS$ ,  $HBr(Br_4)$  requires Br (total), 61·0; Br (labile), 42·6 per cent]. A specimen of the hydropentabromide kept in a weighing bottle overnight, decomposed yielding the *hydrotribromide* of 8-bromo-2-iso-amylamino- $\beta$ -naphthathiazole which had m. p. 121°. [Found: Br (total), 54·8; Br (labile), 27·2.  $C_{16}H_{17}N_2BrS$ ,

HBr ( $\text{Br}_2$ ) requires Br (total), 64.2; Br (labile), 27.1 per cent]. On reduction with sulphurous acid and basification with ammonia, it yielded 8-bromo-2-isoamylamino- $\beta$ -naphthathiazole which had m. p. 126° alone, and when mixed with the specimen obtained from s-4-bromo- $\alpha$ -naphthylisoamylthiocarbamide. (Found: Br, 22.7.  $\text{C}_{16}\text{H}_{17}\text{N}_2\text{BrS}$  requires Br, 22.9 per cent).

(ii) *Synthesis from s-4-Bromo- $\alpha$ -naphthylisoamylthiocarbamide.* s-4-Bromo- $\alpha$ -naphthyliso-amylthiocarbamide. The gum obtained by concentrating a mixture of 4-bromo- $\alpha$ -naphthylthiocarbamide (1 g.) and isoamylamine (0.8 c.c.) in alcohol (7 c. c.) did not solidify after being kept in a vacuum desiccator for 2 days. It was therefore triturated with ether as in the case of the bromonaphthylethyl derivative. The product obtained in this way had m. p. 128° (after sintering at 118°). (Found: Br 22.7.  $\text{C}_{16}\text{H}_{19}\text{N}_2\text{BrS}$  requires Br, 22.7 per cent). A solution of this bromonaphthylthiocarbamide in chloroform (0.2 g. in 4.5 c. c.) was treated with bromine (0.8 c. c. in 0.5 c. c. of chloroform) and the mixture was heated for 5 minutes and concentrated in vacuum. The deep orange crystals of the hydropentabromide obtained in this way were very unstable and rapidly lost bromine yielding the more stable hydrotribromide. [Found: Br (total). 64.0; Br (labile), 42.7 per cent].

8-Bromo-2-isoamylamino- $\beta$ -naphthathiazole hydrotribromide. *Bromination of s- $\alpha$ -Naphthylisoamylthiocarbamide.* A solution of the naphthylthiocarbamide in chloroform (0.2 g. in 4 c. c.) was treated with bromine (0.6 c. c. in 0.6 c. c. of chloroform) and the solution was heated for 5 minutes and thereafter concentrated under reduced pressure at laboratory temperature, when the hydrotribromide separated in yellow crystals, m. p. 121°. [Found: Br (total), 63.9; Br (labile), 27.0 per cent]. On reduction with sulphurous acid and basification with ammonia, it yielded 8-bromo-2-isoamylamino- $\beta$ -naphthathiazole which was identified in the usual way.





# **The Photo-reduction of Alcoholic Solutions of Ferric Chloride in Light.**

BY MATA PRASAD AND P. S. LIMAYE.

Benrath (*J. pr. Chem.*, 1905, 72, 220) has studied the photo-reduction of ferric chloride dissolved in methyl and ethyl alcohols in sun light by measuring the density of the solution at different intervals during exposure to light. The photo-reduction in sun light is more rapid than that in the artificial light so much so that crystals of ferrous sulphate separate out from a concentrated solution of ferric sulphate exposed to sun light (*cf. Benrath, Z. phys. Chem.*, 1910, 74, 115).

Prasad and Sohoni (*J. Indian Chem. Soc.*, 1931, 8, 489) have studied the photo-reduction of ferric chloride dissolved in methyl, ethyl, *n*-propyl and *n*-butyl alcohols in artificial light and have examined the effect of the intensity of the incident light on solutions of different concentrations. They find that in solution in perfectly anhydrous alcohols, the photo-reduction tends to reach a stationary stage but the addition of even slight amount of water causes a reversal of the reaction.

In the following investigation the photo-reduction of ferric chloride dissolved in the above named alcohols has been studied in artificial light for a longer time than that required to reach the equilibrium stage and the order of the photo-reduction has been determined.

## **EXPERIMENTAL.**

### ***The Order of the Photo-reduction of Ferric Chloride in Artificial Light.***

A 1000-Watt Philip's lamp was used as the source of light and the intensity was kept constant by means of a variable resistance placed in series with the lamp. The beam of light rendered parallel by a lens was first passed through a cell (4 cm. thick) containing distilled water to remove the heat radiations before it was incident

on the cell (20 mm.  $\times$  50 mm.) made of optical glass, used to contain the ferric chloride solution. The intensity of the incident light was measured by a Ruben's thermopile connected to a Broca galvanometer and it could be varied by interposing piles of glass plates in the path of the beam.

The solutions were prepared by dissolving B.D.H. anhydrous ferric chloride in Kahlbaum's or Merck's extra pure alcohols which were further purified in the laboratory according to standard methods. 3.6 c.c. of the solution were placed in the reaction cell which was closed by a rubber stopper carrying syphon tubes to remove the solution; the ends of the tubes were closed by pinch cocks and the stopper was made air-tight by coating it with methylated collodion.

The cell was then exposed to light for a certain time at room temperature (28-29°). The optical homogeneity of the solution was maintained by gently shaking it during exposure to light as done by Ghosh and Purkayastha (*J. Indian Chem.*, 1929, 6, 827) and Prasad and Schonl (*loc. cit.*). The reduction of ferric chloride was determined by titrating the solution with *N*/100-potassium dichromate using diphenylamine as an internal indicator (*cf.* Knopp, *J. Amer. Chem. Soc.*, 1924, 46, 253). The volume in c.c. of the dichromate solution required to oxidise the volume of the indicator was first determined and this quantity was subtracted from each titration reading. The effect of alcohols and aldehydes on the titration of ferric salts by potassium dichromate was also studied and a small correction was applied for the presence of alcohols.

In the following tables *T*, *X* and *K* denote the time in minutes, the reduction of ferric chloride in millimoles and the zero-molecular constant respectively. The asterisk (\*) in the following tables indicates the stationary state for which the velocity constants have not been calculated.

TABLE I.

*Solution in pure methyl alcohol.*

Conc. of the solution = 0.118 <i>M</i> .					Intensity = 7.4 cm.				
<i>T</i> /60	...	1	2	3	4	5	6	7	8
<i>X</i> $\times 10^3$	..	2.85	6.15	9.2	12.2	12.35	13.55	16.25	—
<i>K</i> $\times 10^4$	...	4.75	5.18	5.0	5.1	4.72	3.8	3.97	—

TABLE II.

*Solution in pure anhydrous ethyl alcohol.*

Conc. of the solution = 0.115M						Intensity = 25 cm.				
T/60	...	1	2	3	4	5	6	7	8	9
X × 10 <sup>3</sup>	...	2.25	4.45	6.5	5.9	5.25	7.55	8.65	10.35	12.05
K × 10 <sup>4</sup>	...	3.77	3.73	3.61	*	*	2.01	2.06	2.17	2.24

TABLE III.

*Solution in n-propyl alcohol.*

Conc. of the solution = 0.16 M.						Intensity = 7.5 cm.					
T/60	...	1	2	3	3.5	4	4.5	5	6	7	8
X × 10 <sup>3</sup>	...	1.8	3.1	4.85	5.85	6.5	7.05	7.55	8.45	9.36	10.41
K × 10 <sup>4</sup>	...	3.0	2.51	2.69	2.78	2.71	2.61	2.52	2.31	2.23	2.18

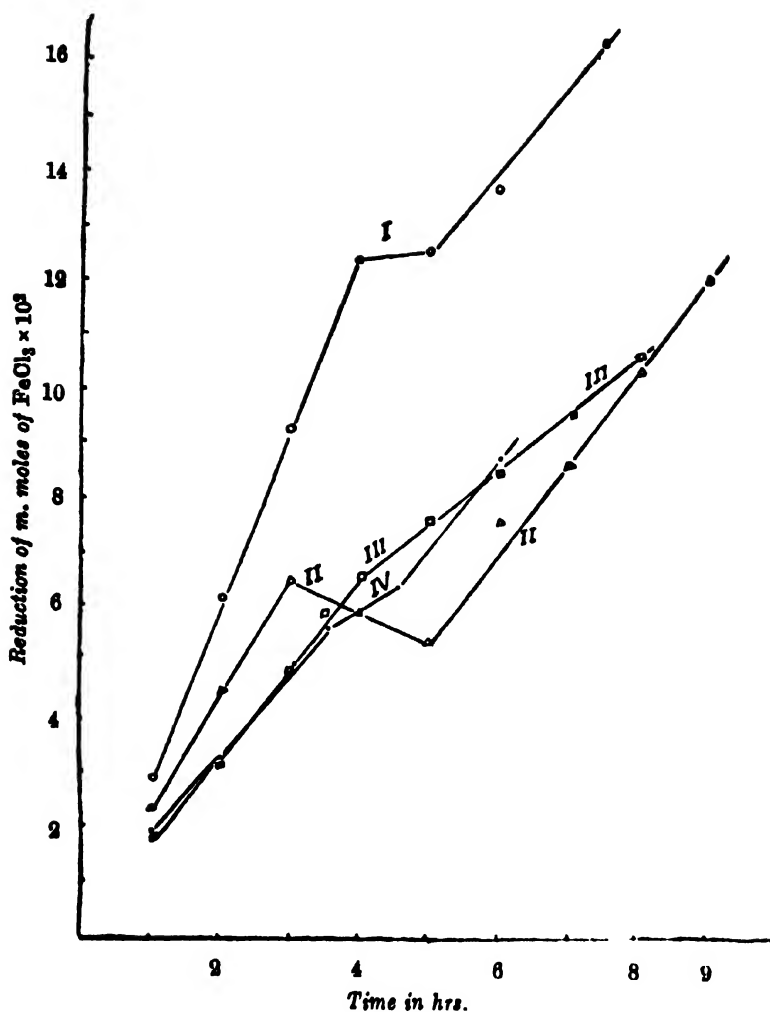
TABLE IV.

*Solution in n butyl alcohol.*

Conc. of the solution = 0.15 M.						Intensity = 25 cm.				
T/60	...	1	2	3	3.5	4	4.5	5	6	
X × 10 <sup>3</sup>	...	1.8	3.15	4.91	5.65	5.85	6.35	7.85	8.65	
K × 10 <sup>4</sup>	...	1.3	2.6	2.73	2.7	..	...	2.62	2.4	

The curves obtained on plotting X against T are shown in Fig. 1. It will be seen that each curve consists of two straight lines separated from each other. This indicates that the photo-reduction proceeds in two stages and the order of the reaction is zero-molecular in both the stages. It is also apparent from the curves that the reaction proceeds faster in the first stage than in the second one.

FIG. 1.



### Extinction Coefficients.

The extinction coefficients of solutions of ferric chloride undergoing reduction were measured in different parts of the visible spectrum with a view to see (a) if any complexes or intermediate compounds of ferric chloride are formed and (b) if any change in the absorption of light by the solution takes place. Nutting's spectrophotometer in conjunction with the Hilger wave-length spectrometer was used. Only solutions in methyl and ethyl alcohols have been examined as these give fairly good reduction on exposure to light.

TABLE V.

*Solution in methyl alcohol.*

Initial conc. of the solution = 0.15 M      Intensity = 7.4 cm.

Time (hrs.)	Extinction coefficients for			
	6220Å	5800Å	5500Å	5300Å
1	0.00	0.16	0.28	0.4
2	0.00	0.12	0.18	0.28
3	0.00	0.115	0.175	0.26
4	0.00	0.11	0.17	0.255
5	0.00	0.04	0.12	0.20
6	0.00	0.01	0.08	0.15
8	0.00	0.00	0.00	0.13

TABLE VI.

*Solution in anhydrous ethyl alcohol.*

Conc. of the solution = 0.18M.      Intensity = 25 cm.

	Extinction coefficients for			
	6220Å	5800Å	5500Å	5300Å
1	0.16	0.22	0.30	0.37
2	0.16	0.21	0.28	0.34
3	0.15	0.22	0.30	0.34
4	0.16	0.22	0.295	0.34
5	0.16	0.22	0.30	0.34
6	0.11	0.17	0.23	0.26
7	0.11	0.15	0.20	0.23
8	0.06	0.10	0.15	0.18
10	0.04	0.06	0.095	0.12

The curve obtained on plotting the values of extinction coefficients against time (Fig. 3, Table V) as well as results in Table VI show that some remarkable change takes place in the solution after the reduction has reached a certain value.

*Effect of the Addition of Ferric Hydroxide Sol to the  
Alcoholic Solutions of Ferric Chloride.*

It is known that hydrolysis of ferric chloride is considerably increased in light (*cf.* Dhar, "Chemical Action of Light," p. 361; and Ritche, *J. Phys. Chem.*, 1928, 32, 1269). It is probable in the present case that ferric chloride may undergo hydrolysis on account of the water formed during the progress of the reaction and this being in a colloidal state may influence the reduction of ferric chloride after some time. The reduction was, therefore, studied by adding 0.5 c.c. of pure ferric hydroxide sol. to 8.5 c.c. of the reaction mixture. The added amount of the sol did not cause any large change (i) in the concentration of the solution and (ii) in the absorption of light by the solution. To note the effect of the colloidal particles alone, a blank experiment was performed with the addition of 0.5 c.c. of distilled water to the ferric chloride solution.

In the following tables  $T$  denotes time in minutes,  $X_1$  and  $X_2$  reduction in millimoles of ferric chloride in the presence of water and the sol. respectively.

TABLE VII.

*Solution in pure methyl alcohol.*

Conc. of the solution = 0.191 M.				Intensity = 7.4 cm.			
$T/60$	...	1	2	3	4	5	6
$X_1 \times 10^3$	...	3.4	7.25	11.1	14.1	14.55	15.6
$X_2 \times 10^3$	...	3.15	4.85	8.85	11.65	12.05	—

TABLE VIII.

*Solution in anhydrous ethyl alcohol.*

* Conc. of the solution = 0.095 M				Intensity = 7.4 cm.		
$T/60$	...	1	2	3	4	5
$X_1 \times 10^3$	...	1.9	3.75	5.25	5.35	6.15
$X_2 \times 10^3$	...	1.65	3.25	4.45	4.45	5.25

TABLE IX.

*Solution in n-propyl alcohol.*

Conc. of the solution = 0.165M.					Intensity = 7.4 cm.	
T/60	...	1	2	3	4	5
$X_1 \times 10^3$	...	1.55	4.15	7.15	8.35	10.15
$X_2 \times 10^3$	...	1.35	3.55	5.35	6.45	8.25

TABLE X.

*Solution in n-butyl alcohol.*

Conc of the solution = 0.091 M.					Intensity = 7.4 cm.	
T/60		1	2	3	4	5
$X_1 \times 10^3$	.	1.35	4.85	7.65	8.95	10.45
$X_2 \times 10^3$	...	1.15	3.35	5.25	6.65	8.45

It will be seen that the colloidal ferric hydroxide inhibits the reduction of ferric chloride and the amount of inhibition increases with the progress of the reduction. The inhibition may be caused by (i) the retarding influence of the colloidal ferric hydroxide or (ii) a diminution in the intensity of light absorbed by the solution due to the screening effect of the colloidal particles.

$X_1$ — $T$  and  $X_2$ — $T$  curves are similar to each other. It, therefore, appears that colloidal ferric hydroxide does not exert any specific influence (a) in causing a change in the course of the reaction from the first to the second stage or (b) in the appearance of the flat part in the curves (Fig. 1) which may be the equilibrium state observed by Prasad and Sohony (*loc. cit.*).

Winther and Oxholt-Howe (*Z. Wiss. Phot.*, 1913, 14, 196), have advanced a theory that at least two different light absorbing molecular species containing ferric ions are present in solutions of ferric chloride in organic acids. As a tentative explanation, it may be considered probable that in the alcoholic solution of ferric chloride a complex containing ferric ion and having a small absorption coefficient is formed as the concentration of the organic substances in the solution increases in course of time. The photo-reduction of this complex or of ferric chloride in the presence of this complex follows a zero order as indicated in the second stage of the reaction.

*Solution of  $\text{FeCl}_3$  in MeOH.*

FIG. 2.

FIG. 3.

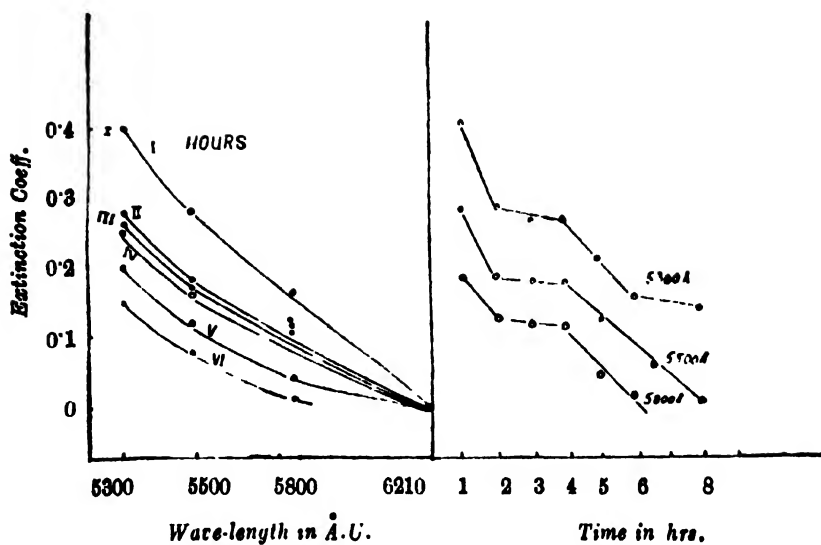
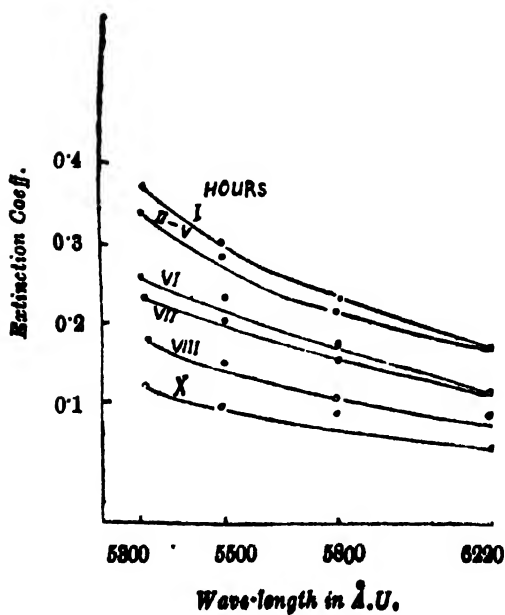
*Solution of  $\text{FeCl}_3$  in EtOH.*

FIG. 4.





The extinction coefficient wave-lengths curves (Figs. 2 and 4) for different exposures of the reaction mixture to light are similar to each other. It appears that the solution containing the complex during the second stage of the reduction behaves towards the change of the extinction co-efficient with wave-lengths in the same way as before the complex is formed. Ghosh and collaborators have shown that the concentration of a complex formed in a photo-chemical reaction can be calculated if the extinction co-efficients of the reactants and of the complex be known. This, however, could not be done in the present case as a large number of substances are present in the solutions of ferric chloride in alcohols undergoing reduction and their concentrations are not known.

THE CHEMICAL LABORATORIES,  
THE ROYAL INSTITUTE OF SCIENCE,  
BOMBAY.

*Received February 13, 1936.*



# Quantum Efficiency of the Photo-reduction of Alcoholic Solutions of Ferric Chloride.

BY MATA PRASAD AND P. S. LIMAYE.

In a previous communication (*J. Indian Chem. Soc.*, 1938, 10, 91) it has been shown that for the first four hours the order of the photo-reduction of alcoholic solutions of ferric chloride in artificial light is zero molecular. In the present investigation the quantum efficiency of the photo-reduction of ferric chloride has been studied in radiations of different wave-lengths at different temperatures. The effect of the concentration of the solution on the quantum efficiency has also been studied and the applicability of the Einstein's Law of photochemical equivalence has been discussed.

## EXPERIMENTAL.

The experimental arrangement was the same as described in the previous paper (*loc. cit.*). The quantum efficiency was studied at three different temperatures, 30°, 38°, and 45°. The temperature was maintained constant by an electrically heated air thermostat within  $\pm 0.05^\circ$ . The reaction cell was well protected from the radiations from the heater by means of a black screen interposed between the reaction cell and the heater. It was observed from the absorption photographs of ferric chloride solutions in ethyl alcohol that complete absorption between 4000Å and 5000Å takes place if the concentration of the solution is not less than 0.08M. Consequently solutions of concentrations greater than 0.08M were used for the measurements of quantum efficiency. The quantum efficiency was studied in the radiations 4000Å–5000Å (mean value 4500Å) and 4580Å–4940Å (mean value 4760Å). These radiations were obtained by using the following solution filters:

(a) 2.716N  $\text{CuSO}_4$  + 0.01 g. methyl violet in 100 c. c. of water, each in 1 cm. thickness. Transmission 4000Å – 5000Å.

(b)  $\text{CuSO}_4$  aq., 150 g./litre 2 cm. thickness + methyl green aq. 0.1 g./litre 2 cm. thickness. Transmission 4580Å – 4940Å.

The amount of reduction was measured by titrating the solution with  $N/100$ -dichromate solution using diphenylamine as an internal indicator.

To measure the light energy absorbed by the solution, the galvanometric deflections obtained by exposing a large surface thermopile connected to a sensitive galvanometer were first calibrated in terms of Hefner-100. The energy in Hefner-100 absorbed by the solution was then calculated from the deflections of the galvanometer for pure alcohol and for the solution of ferric chloride in that alcohol.

The number of molecules changed per sq. cm. per sec. was calculated from the titration data using the formula,

$$N \times n \times t \times A$$

where  $N$  is the Avogadro's constant ( $6.06 \times 10^{23}$ ),  $n$  the number of g. molecules of ferric chloride reduced in time  $t$ , expressed in seconds and  $A$  (7 sq. cm.), the area of the solution, illuminated by light.

The number of quanta absorbed per sq. cm. per sec. is given by the formula,

$$e \times 900 \times \lambda \times 10^{-8} / 3 \times 10^{10} \times 6.5 \times 10^{-27}$$

where  $e$  is the absorption in Hefner-100 and  $\lambda$  the mean wave-length of the filter in Angstrom units.

The quantum efficiency  $Q$  was calculated from

$$Q = \frac{\text{No. of molecules changed}}{\text{No. of quanta absorbed}}$$

TABLE I.

*Solution in pure methyl alcohol.*

Conc. of the solution = 0.188M.

Mean wave-length = 4500Å.			Mean wave-length = 4760Å.		
Temp.	Temp. coeff.	Q.	Temp.	Temp. coeff.	Q.
30°	1.31	1.28	30°	1.53	0.78
35°		1.61	35°		1.18
45°	1.7	3.86	45°	1.65	1.89

TABLE II.

*Solution in pure methyl alcohol.*

Conc. of the solution = 0.094M.

Mean wave-length = 4500Å.			Mean wave-length = 4760Å.		
Temp.	Temp. coeff.	Q.	Temp.	Temp. coeff.	Q.
30°	...	0.64	30°	...	0.32
	1.1			1.7	
38°		0.68	38°		0.68
	2.7			2.2	
45°		1.91	45°		1.125

TABLE III.

*Solution in anhydrous ethyl alcohol.*

Conc. of the solution = 0.19M.

Mean wave-length = 4500Å.			Mean wave-length = 4760Å.		
Temp.	Temp. coeff.	Q.	Temp.	Temp. coeff.	Q.
30°		1.24	30°		0.49
	1.2			1.3	
38°		1.55	38°		0.613
	1.8			2.04	
45°		2.77	45°		1.25

TABLE IV.

*Solution in anhydrous ethyl alcohol.*

Conc. of the solution = 0.095M.

Mean wave-length = 4500Å.			Mean wave-length = 4760Å.		
Temp.	Temp. coeff.	Q.	Temp.	Temp. coeff.	Q.
30°		0.58	30°		0.3
	1.2			1.5	
38°		0.69	38°		0.37
	2.4			1.7	
45°		1.69	45°		0.48

TABLE V.

*Solution in n-propyl alcohol.*

Conc. of the solution = 0.155M.

Mean wave-length = 4500Å.			Mean wave-length = 4760Å.		
Temp.	Temp. coeff.	Q.	Temp.	Temp. coeff.	Q.
30°		2.08	30°		0.59
	1.23			1.3	
38°		3.67	38°		0.77
	1.1			1.1	
45°		3.98	45°		0.89½

TABLE VI.

*Solution in n-propyl alcohol.*

Conc. of the solution = 0.08M.

Mean wave-length = 4500Å.			Mean wave-length = 4760Å.		
Temp.	Temp. coeff.	Q.	Temp.	Temp. coeff.	Q.
30°		1.55	30°		0.34
	1.23			1.3	
38°		2.2	38°		0.44½
	1.03			1.1	
45°		2.26	45°		0.46

TABLE VII.

*Solution in n-butyl alcohol.*

Conc. of the solution = 0.165M.

Mean wave-length = 4500Å.			Mean wave-length = 4760Å.		
Temp.	Temp. coeff.	Q.	Temp.	Temp. coeff.	Q.
30°		2.5	30°		0.75
	1.46			1.08	
38°		3.64	38°		0.77½
	1.2			1.0	
45°		4.34	45°		0.82

TABLE VIII.

*Solution in n-butyl alcohol.*

Conc. of the solution = 0.082M.

Mean wave-length = 4500Å.			Mean wave-length = 4760Å.		
Temp.	Temp. coeff.	Q.	Temp.	Temp. coeff.	Q.
30°		1.907	30°		0.56
	1.0			1.0	
38°		1.91	38°		0.501
	1.2			0.92	
45°		2.26	45°		0.56

## DISCUSSION.

It will be seen from the foregoing tables that the quantum efficiency in dilute solutions is much less than that in the concentrated ones and that at the same temperature the quantum efficiency of the same solution is greater in light of lower wave-lengths and it increases as the temperature is raised. The results are in agreement with those usually obtained in photochemical reactions (*cf.* Dhar and Bhattacharya, *J. Indian Chem. Soc.*, 1929, 6, 143; Mukerji and Dhar, *J. Phys. Chem.*, 1931, 6, 1790; and Allmand, *J. Chem. Soc.*, 1931, 1652).

It is also apparent from the tables that the quantum efficiency of the photo-reduction of ferric chloride in different alcohols varies from nearly 0.6 to 4. It appears therefore that Einstein's Law is valid approximately in the present case. The primary effect of the absorption of a light quantum appears to be the excitation of the ferric chloride molecules which break up into ferrous chloride and chlorine. No other side reaction seems to take place during the first two hours of the starting of the reaction.

The authors are very thankful to Mr. S. M. Mehta, B.A., M.Sc. for his kind assistance.

THE CHEMICAL LABORATORIES,  
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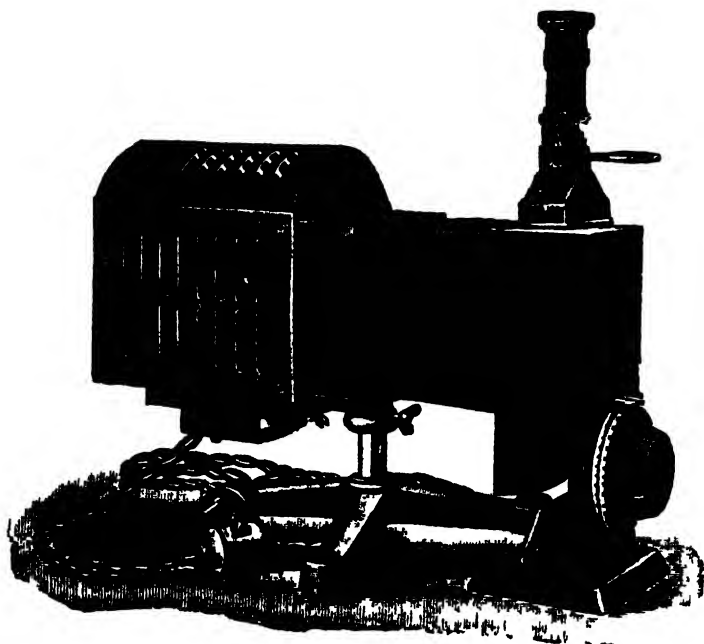
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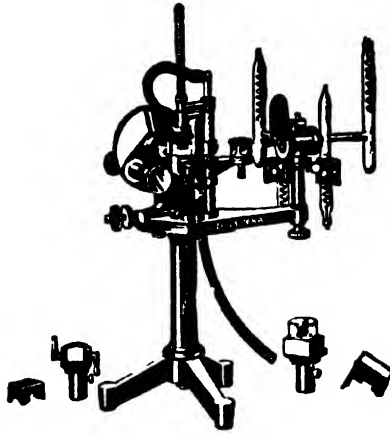
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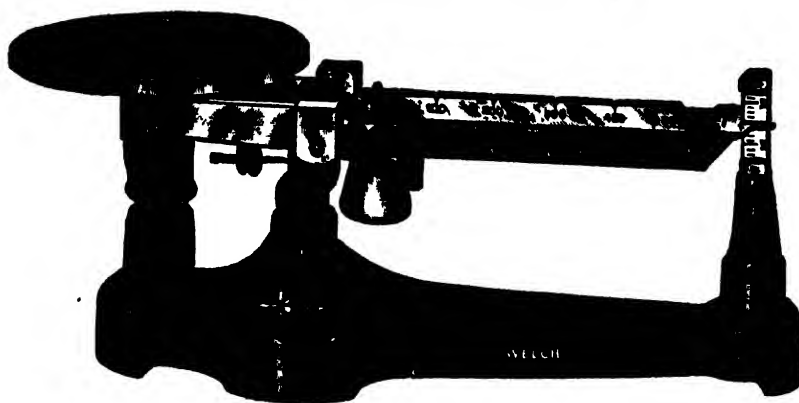
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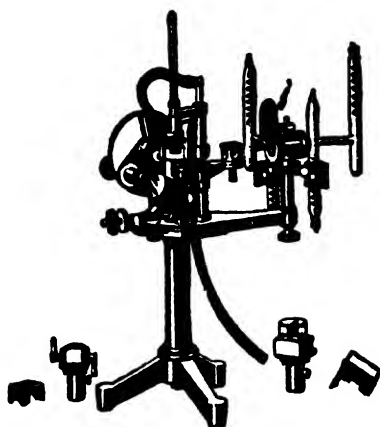


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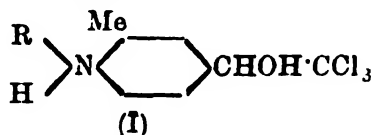
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## The Condensation of Methyl- and Ethyl-*o*-toluidines with Chloral Hydrate.

BY A. N. MELDRUM AND A. H. ADVANI.

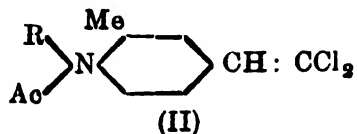
Boessneck (*Ber.*, 1887, 20, 3193 ; 1888, 21, 782) condensed monomethylaniline, monoethylaniline, dimethylaniline and diethylaniline with chloral hydrate and assumed that the chloral group enters the *para* position to the amino group.

The condensation products of methyl-*o*-toluidine and of ethyl-*o*-toluidine with chloral hydrate, (I, R=CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>) have now



been prepared by mixing the components in molecular proportions, adding anhydrous zinc chloride as a condensing agent and shaking for 48 hours in an automatic shaker. The solid hydrochlorides obtained after treating the mixture with concentrated hydrochloric acid were converted into the bases by treatment with strong ammonia.

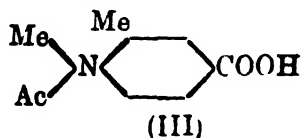
The condensation products yielded nitrosoamines and acetyl derivatives. The compound (I) forms both mono- and diacetyl derivatives, both the OH and NH groups being acetylated. These acetyl derivatives produced the compound (II) on reduction with zinc dust



and acetic acid, while (I) is not thus reduced. The unsaturated formula  $-\text{CH}=\text{CCl}_2$ , as suggested by Jocitsch (*J. Russ. Chem. Soc.*, 1898, 30, 920, 990-1003) from the reduction of compounds of this type is preferred to the saturated formula  $-\text{CH}_2 \cdot \text{CHCl}_2$  according to Meldrum and Alimchandani (*J. Indian Chem. Soc.*, 1925, 2, 1). Recent work by Yelburgi and Wheeler (communicated to this Journal) has shown that the unsaturated formula is correct with compounds of this type and here the hydrogen analysis definitely favours the unsaturated formula.

The fact that the monoacetyl derivative and its reduction product cannot be converted into a nitrosoamine and that the reduction of the chloral chain of the monoacetyl derivative does not remove the acetyl group proves that on acetylation of (I) the NH group is first acetylated.

To prove that the chloral chain occupies the *para* position to the amino group, oxidation of (I), the mono- and diacetyl derivatives by means of alkaline potassium permanganate was tried. The first two substances did not give pure products. A monobasic acid (III)



melting at 232° was, however, obtained from the diacetyl derivative, which on hydrolysis with 40% potassium hydroxide solution under pressure at 150° produced *p*-methylamino-*m*-toluic acid melting at 201°. This acid was synthesised for mixed melting point determination by the method of Houben (*Ber.*, 1900, **42**, 4490)

#### EXPERIMENTAL.

*p*-( $\alpha$ -Hydroxy- $\beta$ -trichloroethyl)-methyl-*o*-toluidine hydrochloride.—Equimolecular amounts of methyl-*o*-toluidine (25 g.) and chloral hydrate (35 g.) were mixed and dry powdered zinc chloride (5 g.) added after all the chloral hydrate had gone into solution. The mixture was shaken for 72 hours when it formed a deep green sticky mass. It was heated on a water-bath at 60° for 4 hours and treated with excess of concentrated hydrochloric acid, when the solid hydrochloride of the condensation product separated after keeping for 24 hours in a refrigerator. This was filtered off under suction, washed with concentrated hydrochloric acid and dried on a porous plate, yield 13 g. (73%). It was crystallised from 10% ethyl alcohol containing traces of hydrochloric acid and basified with strong ammonia (*vide infra*). The base after crystallising from dilute methyl alcohol was again treated with concentrated hydrochloric acid with a view to obtain a purer specimen of the hydrochloride. This was recrystallised from dilute ethyl alcohol, m.p. 207–8° (decomp.). (Found: Cl, 46.7.  $C_{10}H_{13}ONCl_4$  requires Cl. 46.6 per cent).

The hydrochloride was converted into the base by grinding the substance in a mortar with strong ammonia. A light green sticky mass



was first obtained which solidified after grinding for 10 minutes and keeping in the ammoniacal solution for 2 hours. The solid mass was powdered, washed well with water and crystallised from methyl alcohol and water as rhombic plates, m.p. 104.5°. (Found: Cl, 39.6.  $C_{10}H_{12}ONCl_3$  requires Cl, 39.6 per cent).

The *monoacetyl* (*N*-acetyl) derivative was prepared by heating the base (5 g.) with acetic anhydride (15 c.c.) containing a few drops of concentrated sulphuric acid on the water-bath for a few minutes. On keeping overnight the solution was poured over crushed ice and the white solid was washed well with hot water and crystallised from methyl alcohol, m.p. 187°, yield 4.1 g. (Found: Cl, 34.2.  $C_{12}H_{14}O_2NCl_3$  requires Cl, 34.3 per cent).

The *diacetyl* derivative was obtained by heating the base with acetic anhydride on the water-bath for 4 hours. The oil, obtained after the solution was poured over crushed ice, solidified on grinding with cold dilute sodium carbonate solution, washing with cold water and keeping in a refrigerator for 24 hours. It was crystallised from methyl alcohol, m.p. 111°, yield 5.4 g. (83.7%). (Found: Cl, 30.2.  $C_{14}H_{16}O_3NCl_3$  requires Cl, 30.2 per cent).

The *nitrosoamine* derivative was prepared by adding sodium nitrite solution (25 %) to a cooled solution of the base in a small quantity of absolute alcohol containing a little HCl, when a white precipitate was obtained. The mixture was kept in a freezing bath for 2 hours and the product thus formed was washed with cold water and crystallised from methyl alcohol, m.p. 172.3° (decomp.). (Found: C 37.0.  $C_{10}H_{11}O_2N_2Cl_3$  requires Cl, 35.8 per cent).

*p*-( $\beta$ -Dichloroethylene)-*o*-*N*-methyl acetotoluidide.—The monoacetyl derivative (40 g.) was suspended in glacial acetic acid (70 c.c.) contained in a glass-stoppered bottle, and zinc dust (11 g.) was added gradually while the mixture was shaken, keeping the temperature at about 40°. After 5 hours the mixture was filtered under suction and the filtrate on dilution and subsequent partial neutralisation with sodium carbonate gave a colourless oil, which was extracted with ether, washed several times with water and distilled at 204°/11 mm. It solidified after keeping for 5 days in a vacuum desiccator containing alkali. The solid was washed with petroleum ether and crystallised from methyl alcohol, m.p. 107.8°, yield 1.5 g. (5%). The same compound was obtained by the reduction of the diacetyl derivative. (Found: Cl, 27.8.  $C_{12}H_{13}ONCl_2$  requires Cl, 27.5 per cent).

*p*-N-Methylacetyl-amino-*m*-toluic acid.—The diacetyl derivative (10 g.) was suspended in dilute potassium hydroxide solution and a solution of potassium permanganate (3 g; 1.5%) was added gradually, the mixture shaken for 24 hours and then heated on a water-bath (3 hours), when the solution was completely decolourised. The liquid, filtered from the precipitated hydrated manganese dioxide, was concentrated and acidified with strong HCl and the precipitate crystallised from boiling water as white needles, m.p. 232°, yield 2.8 g. (50.5%). (Found: N, 6.8; Eq. wt., 206.  $C_{11}H_{13}O_3N$  requires N, 6.8 per cent; Eq. wt., 207).

*Hydrolysis of p*-N-methylacetyl-amino-*m*-toluic acid.—Many unsuccessful attempts were made to hydrolyse this acid by means of concentrated hydrochloric acid and by potassium hydroxide at temperatures up to 100°. Eventually the acid (3 g.) was dissolved in 40% potassium hydroxide solution (6 c.c.) and heated at 150° for 6 hours in a sealed tube. The product was dissolved in dilute HCl and the acid precipitated with sodium acetate. It was washed with a little cold water and crystallised from boiling water as white needles, m.p. 201°; soluble in dilute hydrochloric acid and dilute sodium hydroxide. The compound was found to be identical with *p*-N-methylamino-*m*-toluic acid (m.p. 201°), synthesised by the method of Houben (*loc. cit.*), the mixed m.p. being 200°.

*p*-( $\alpha$ -Hydroxy- $\beta$ -trichloroethyl)ethyl-*o*-toluidine hydrochloride was obtained from ethyl-*o*-toluidine and chloral as small rhombic plates from dilute ethyl alcohol, m.p. 210-12° (decomp.). (Found: Cl, 44.4.  $C_{11}H_{15}ONCl_4$  requires Cl, 44.5 per cent).

The free base, obtained from the hydrochloride by treatment with ammonia, crystallised from carbon tetrachloride, m.p. 107°. (Found: Cl, 37.9.  $C_{11}H_{14}ONCl_3$  requires Cl, 37.7 per cent).

The nitrosoamine, obtained in the usual manner, crystallises as thick square plates from benzene, m.p. 138° (decomp.). (Found: Cl, 34.3.  $C_{11}H_{13}O_2N_2Cl_3$  requires Cl, 34.1 per cent).

The diacetyl derivative was prepared in the same way as the diacetyl derivative of *p*-( $\alpha$ -hydroxy- $\beta$ -trichloroethyl) methyl-*o*-toluidine. It was crystallised from dilute alcohol, m.p. 106-7°. (Found: Cl, 29.2.  $C_{15}H_{18}O_3NCl_3$  requires Cl, 29.0 per cent).

# Studies on the Decompositions and Reactions of Urea.

## Part I. Reactions of Urea with Hydrazines, Aldehydes, Ketones, etc.

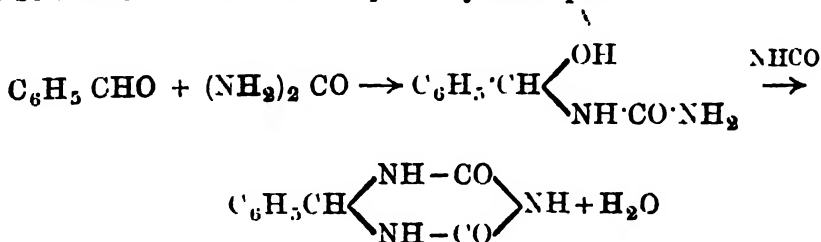
BY JNANENDRA MOHON DAS-GUPTA.

From a study of the literature it appears that the true mechanism of the reactions of urea has in many cases been little studied. The following investigations, while throwing considerable light in this respect, also point to the importance of urea as a convenient source of both ammonia and isocyanic acid, which can be successfully utilised in many reactions and syntheses. The advantages of urea as a source of  $\text{NH}_3$  and  $\text{NHCO}$  are (i) ammonia can be obtained in perfectly dry state; (ii) both ammonia and isocyanic acid can be made to evolve at very high temperatures up to  $200^\circ$  or above; (iii) as they are generated *in situ*, they act in the nascent state and are, therefore, much more reactive.

Reactions of hydrazines with urea have been investigated in the dry state by Pinner (*Bcr.*, 1887, 20, 2358), Skinner and Ruhemann (*J. Chem. Soc.*, 1888, 47, 550) and others but in aqueous solutions also similar results have been obtained here. The mechanism of the former type of reactions has been supposed to be of the nature of direct condensation of one or two molecules of urea with the base (hydrazine) followed by the splitting of ammonia. The fact that semicarbazide and hydrazine dicarbonamide are obtained by heating hydrazine with urea (*J. pr. Chem.*, 1895, ii, 52, 466) below the decomposition point of the latter in the solid state, appears to support the above mechanism. But, since urea decomposes into ammonia and isocyanic acid much below its melting point in various solvents (such as water, alcohol, glycerine, etc., as can be shown by warming with silver nitrate when  $\text{AgCNO}$  is produced), it is quite probable that in the above cases as well, hydrazine hydrate acts as a dissociating medium, and the reactions actually take place between the hydrazine base and the isocyanic acid produced under such condition. The fact that hydrazines yield similar products

even in aqueous solutions, lends support to these interpretations of the reactions.

By gradually heating benzaldehyde with urea, Schiff (*Annalen*, 1896, 291, 376) obtained benzylidenecarbamide and by further heating above its melting point (up to 220°) ammonia was split off and benzylidenebiuret was produced. But by simply heating the reactants at 150-60° only, the same compound has been obtained. So the mode of its formation under this latter condition appears to be different. The reaction probably takes place thus:



Since benzylidenecarbamide does not decompose below its melting point (200°), the formation of benzylidenebiuret direct from it with splitting off of ammonia at 150-60° appears to be unlikely.

Reactions of urea with aromatic haloid substitution products appear to have been very little investigated. By the action of alcoholic ammonia on polynitrohalides at high temperatures in sealed tubes, corresponding amines have usually been obtained. It is quite natural to expect that urea, which is an excellent source of ammonia at very high temperatures, should also yield similar products with polynitrohalides. This expectation has been fulfilled.

By similar reactions with nitrophenols, corresponding amines have been obtained in several cases by Kym (*J. pr. Chem.*, 1907, ii, 75, 325). This reaction has been extended to the case of other phenols.

#### EXPERIMENTAL.

##### *Reactions of Hydrazines and Hydroxylamine with Urea.*

**Phenylhydrazine hydrochloride and urea.**—Phenylhydrazine hydrochloride (1.4 g.), urea (0.7 g.) and water (7.8 c.c.) were heated together on water-bath for 2½ hours; the mixture cooled and the precipitate obtained on rubbing crystallised from alcohol. It melted at 172°; the melting point being not depressed when mixed with a sample prepared from phenylhydrazine hydrochloride and potassium cyanate.

*asym-Phenylbenzylhydrazine hydrochloride and urea.*—A mixture of *asym*-phenylbenzylhydrazine hydrochloride (2 g.), urea (1.5 g.) and water (10 c.c.) was heated on a water-bath (2-2½ hours). The precipitated semicarbazide was purified by dissolving in chloroform and re-precipitating by ether. It melts at 139-40° (*cf.* Milrath, *Ber.*, 1908, 41, 1665).

*8 Quinolylhydrazine and urea.*—8-Quinolylhydrazine (1.4 g.) and urea (1.2 g.) were mixed together and heated at 150-60° for ¼ hour. The mass, after extraction with warm water and washing with ether, was crystallised from alcohol, m. p. 230° (decomp.). Beilstein reports 235° (decomp.). The same compound was obtained by heating the dihydrochloride of 8-quinolylhydrazine (1.1 g.) with excess of urea (0.9 g.) in aqueous solution as in the previous cases.

*Hydrazine hydrochloride and urea.*—A mixture of hydrazine hydrochloride (1.1 g.), urea (2 g.) and water (7-8 c.c.) was refluxed for about 1½ hours. The precipitate, obtained on concentrating the solution, was warmed with ether and crystallised from hot water; m.p. 246° with decomposition. (Hydrazine dicarbonamide).

Hydrazine dicarbonamide was also produced from hydrazine hydrate (1 c. c.) and urea (2 g.) dissolved in water (7-8 c. c.) and heating the mixture for 2½ hours. The solution was then concentrated to a small bulk, when hydrazine dicarbonamide crystallised out.

*Hydroxylamine hydrochloride and urea.*—Hydroxylamine hydrochloride (1 g.), urea (1 g.) and water (8-9 c.c.) were heated together on water bath for 2 hours. Bubbles of gas evolved from the solution throughout the reaction. The solution gave strong bluish violet coloration with ferric chloride solution, which showed that hydroxy-urea was formed but it could not be easily isolated. By dry heating a mixture of the two reactants gradually to about 145°, the mass swelled up and gases were given out with explosive violence. No hydroxyurea could be detected in the solid residue.

#### *Reactions of Aldehydes and Ketones with Urea.*

*Benzylidenebiuret.*—Benzaldehyde (1 g.) and urea (1.2 g.) were heated together at 150-60° (1½ hours) in an oil bath. The melt was then cooled, washed repeatedly with warm water and the light yellow precipitate filtered. It was next washed several times with warm alcohol and was thus obtained as a white powder almost insoluble in water, alcohol and ether. It was crystallised from hot

water, m. p.  $270^{\circ}$  (decomp.). (Found: N, 21.54.  $C_9H_9O_3N_3$  requires N, 21.99 per cent).

**4'-(Dimethylamino)-benzylidenebiuret.**—An intimate mixture of *p*-dimethylaminobenzaldehyde (1.4 g.) and urea (1.4 g.) was heated at  $160^{\circ}$  for about 2 hours. The mass was washed with hot water and filtered, when a yellowish precipitate was obtained. It was dissolved in dilute hydrochloric acid, charcoaled and reprecipitated with alkali. The precipitate was repeatedly washed with warm alcohol and was obtained as a white powder, m. p.  $264^{\circ}$  (decomp.). It is insoluble in water, ether and acetone. (Found: N, 23.42.  $C_{11}H_{14}O_2N_4$  requires N, 23.92 per cent).

**2'-Hydroxybenzylidenebiuret.**—A mixture of salicylaldehyde (1 g.), and urea (1 g.) was heated at  $150-60^{\circ}$  for  $1\frac{1}{2}$  hours. The cold mass was next well-powdered and dissolved in dilute alkali. The filtrate was acidified with dilute hydrochloric acid and the yellow precipitate washed repeatedly with water and warm alcohol. The light yellow insoluble residue was further purified by redissolving in dilute alkali. The clear filtrate was then charcoaled, reprecipitated with dilute acid and the white precipitate of 2'-hydroxybenzylidenebiuret thus obtained was further washed with alcohol. It is practically insoluble in water, ether and alcohol and does not melt below  $280^{\circ}$ . (Found: N, 19.82.  $C_9H_9O_3N_3$  requires N, 20.29 per cent).

**1-Methylbenzylideneurea.**—Acetophenone and urea did not appreciably react under the above conditions. But by carrying out the reaction at higher temperature and for a longer period the desired compound was obtained. Acetophenone (1.2 g.) and urea (1.2 g.) were heated together at  $180-85^{\circ}$  for 3-4 hours. The melt was repeatedly extracted with boiling water. The solid-residue was powdered, repeatedly washed with ether and crystallised from alcohol, m. p.  $176^{\circ}$ . It is soluble in alcohol and insoluble in water, ether, acids and alkalis. (Found: C, 59.5; H, 6.6; N, 15.20.  $C_9H_{10}ON_2 \cdot H_2O$  requires C, 60.0; H, 6.65; N, 15.55 per cent).

Diphenylketone and urea did not appreciably react under the above conditions.

#### *Reactions of Aromatic Halogen Compounds with Urea.*

**2:4-Dinitrobromobenzene and urea.**—An intimate mixture of 2:4-dinitrobromobenzene (1.2 g.) and urea (2 g.) was heated at  $200^{\circ}$  for about 4 hours. The yellow crystalline mass was well powdered

and repeatedly washed with hot water and crystallised from alcohol as a glistening yellow crystalline mass, m. p.  $181.82^{\circ}$ , yield 60%. It was found identical with the compound obtained from the above nitro derivative and alcoholic ammonia (Clemm, *J. pr. Chem.*, 1879, ii. 1, 175). (Found: N, 22.82.  $C_6H_5O_4N_3$  requires N, 22.95 per cent).

The corresponding carbamido derivative, resulting from the direct condensation of the bromo compound with urea was also formed to some extent, but remained undissolved in alcohol. In the case of 2:4-dinitrochlorobenzene, the yield of the amine was 70%.

*2:6-Dinitrochlorobenzene and urea.*—On heating an intimate mixture of the above chlorobenzene derivative with large excess of urea as in the previous case, 2:6-dinitroaniline was formed, which was separated and purified as before; yellow needles, m. p.  $138^{\circ}$ , yield 65%. From the corresponding iodo derivative, a 60% yield of the amine was obtained.

*3:5-Dinitrochlorobenzene and urea* yielded 3:5-dinitroaniline, which crystallised from alcohol in yellow needles, m. p.  $158^{\circ}$ , yield 30%. (Found: N, 22.90.  $C_6H_3O_4N_3$  requires N, 22.95 per cent).

#### *Reactions of Phenols with Urea.*

*2:6-Dinitrophenol and urea.*—An intimate mixture of 2:6-dinitrophenol (1 g.) and urea (2 g.) was heated at  $200^{\circ}$  for 4-5 hours. The dirty black mass was well powdered, repeatedly extracted with hot water and the residue washed with dilute alkali and crystallised from alcohol as yellow needles, m. p.  $138^{\circ}$ , yield 45%.

*3:5-Dinitrophenol and urea* under the above conditions yielded 3:5-dinitroaniline, which was crystallised from alcohol in yellow needles, m. p.  $158^{\circ}$ . The yield was very poor.

*2:5-Dinitrophenol and urea* similarly gave 2:5-dinitroaniline as orange-yellow crystals from alcohol, m. p.  $137^{\circ}$ , yield 25%. (Found: N, 22.9.  $C_6H_3O_4N_3$  requires N, 22.95 per cent).

The author is indebted to Dr. U. N. Brahmachari for the facilities he has given for carrying out these investigations.



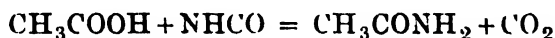


# Studies on the Decompositions and Reactions of Urea.

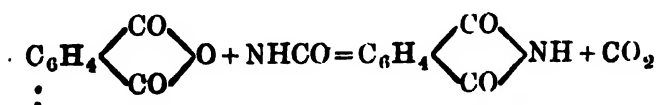
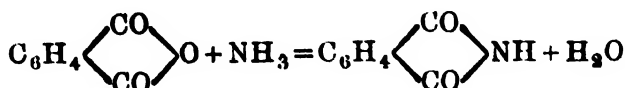
## Part II. Reactions of Urea with Acids, Anhydrides, etc.

BY JNANENDRA MOHON DAS-GUPTA.

As a typical case of the reaction of urea with an acid, may be discussed its action on acetic acid at the boiling point of the latter. When urea is boiled with the acid with a few crystals of silver nitrate for a short time, a precipitate of silver cyanate (which can be tested by the hydroxylamine hydrochloride-ferric chloride reaction) is formed. No silver cyanate is formed on adding silver nitrate solution at the end of the reaction. This shows that cyanic acid, which is produced under such condition, immediately reacts with the acid thus,

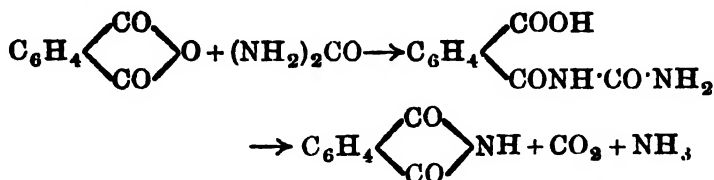


while the ammonia produced forms ammonium acetate. Evolution of  $\text{CO}_2$  has been noticed to be continuous from the very outset. That, besides acetamide, ammonium salt is also formed may be easily seen by cooling a part of the mixture and adding alkali, when ammonia is evolved. Aromatic monobasic acids, however, do not yield the corresponding amides under similar conditions. Formation of imides in the case of dibasic aromatic acids is probably due to dehydrating action of cyanic acid whereby corresponding anhydrides are formed first, which latter then react with ammonia and excess of isocyanic acid thus:



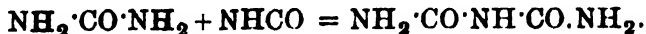
The results obtained by Werner (*J. Chem. Soc.*, 1916, 109, 1120) in the case of acetic anhydride, while supporting the above

scheme, would show that the formation of the imide on the line of Piuti (*Annalen*, 1882, 214, 20) and Dunlop (*Amer. Chem. J.*, 1896, 18, 332) may take place only to a small extent under the studied conditions.



Formation of an ureide in the case of cinnamic acid appears to be exceptional.

Esters and amides have been found to remain unreacted by urea at high temperature (150°-180°), without yielding amides and ureides respectively with the ammonia and isocyanic acid produced. But urea regarded as an amide (carbamide) yields, when heated alone, about 20% biuret thus,



Several reactions of urea in aqueous solution have been studied. It is interesting to study and compare its reactions in other solvents, *e. g.*, alcohol, glycerol and acetic acid, in which similar decomposition into ammonia and isocyanic acid have already been noticed. The temperature at which the dissociation takes place to an appreciable extent depends on the solvent. In the case of alcohol, it is approximately 82°, in the case of glycerol 100°, in the case of acetic acid 110° and in the case of water 80-85°. Since alcohol increases the rate of formation of ammonium cyanate into urea, urea is very little decomposed at its boiling point; hence very poor yields are obtained in such solution.

The reactions of urea with various bases in acetic acid solution are usually supposed to be due to the direct elimination of two molecules of ammonia from one molecule of urea and two of the base. The fact that urea dissociates into ammonia and isocyanic acid in acetic acid solution and also that phenylurea alone decomposes in the same solvent into diphenylurea, makes it more probable that the above reaction takes place thus,



Phenylurea, thus formed, then decomposes into phenyl isocyanate and ammonia (Davis and Underwood, *J. Amer. Chem. Soc.*, 1922, **44**, 2595) which then combine to form diphenylurea.

### EXPERIMENTAL.

#### *Reactions of Acids and Anhydrides with Urea.*

In most of these reactions, the mixtures are heated at 150-170° and then cooled and washed with small amounts of water. The residue is washed with dilute ammonia or alkali. The aliphatic imides are either extracted with some solvents or recovered by distillation. Aromatic imides are obtained in practically pure state by simply washing with dilute ammonia or alkali. Excess of urea is used in most of the cases, while with lesser amounts some of the acids or anhydrides remain unreacted. Relative proportions of the ammonium salts and amides formed also depend to some extent on the amount of urea used and also on the temperature and duration of heating. The results have been shown in Tables I—III.

*Decomposition of phenylurea in acetic acid solution.*—A mixture of phenylurea (1 g.) and glacial acetic acid (5-6 c. c.) was gently refluxed for about 1 hour. It was next cooled and diluted with water, when a crystalline precipitate of diphenylurea separated out. On recrystallisation from alcohol, it melted at 235°. (Found: N, 13·0.  $C_{13}H_{12}ON_2$  requires N, 13·2 per cent).

*Reactions of urea in various solvents.*—Reactions of urea in glycerol were carried at 120°, in acetic acid at 117°, in water at 95-100° (except where stated), usually for 2 hours and in alcohol at 82° for 5 hours. Yields in 50% alcoholic solution were always greater than in 95% alcohol but these were small in both cases. The products were obtained by distilling off the alcohol under reduced pressure. From glycerol and acetic acid solutions, these were separated by diluting with water and proceeding in the usual way. The results are given in Table IV.

TABLE I.  
*Reactions of Monobasic Acids with Urea.*

(A = Acid used; U = Urea).

Acid used.	Reaction and isolation.	Products formed.	M.p. and mixed m.p.	Remarks and analysis.
*Acetic acid ...	A (5 g.) + U (5 g.), refluxed for 2 hours and then distilled	Acetamide, ammonium acetate	82°	Little ammonium acetate also collects in the condenser. CO <sub>2</sub> is given out. Yield of the amide 30%.
Propionic acid ...	A (7.2 g.) + U (6 g.) refluxed for 2½ hours and then distilled	Propionamide, ammonium propionate	79°	Distillate above 170° collected.
Phenylacetic acid ...	A (1.4 g.) + U (6 g.), heated at 150°-160° for 1½ hours	Phenylacetamide, ammonium phenylacetate	156°	Yield of amide 50%.
Cinnamic acid ...	A (4 g.) + U (1 g.), heated at 160°-170° for 1-1½ hours	Cinnamoyl urea, ammonium cinnamate	218°-19°	(Found : C, 62.8; H, 5.11; N, 14.5. Calcd. C, 63.16; H, 5.26; N, 14.73%). Crystallised from alcohol as shining flakes, yield 0.5 g.
Benzoic acid ...	Heated at 150° or 170° with different proportions of urea	Ammonium benzoate		No benzamide formed. Small amount of ammonium benzoate collected in the cooler part when excess of acid is used. Benzoic acid is obtained on acidifying the filtrate.
Salicylic acid ...	A (2.6 g.) + U (1.2 g.), heated at 150°-160° for 2 hours	Ammonium salicylate		No amide formed. Salicylic acid obtained by acidifying the filtrate.

TABLE II.

## Reactions of Dibasic Acids with Urea.

(A = Acid used; U = Urea).

Acid used.	Reaction and isolation.	Products formed.	M.p. and mixed m.p.	Remarks and analysis.
Oxalic acid. (crystallised)	A (2.4g.) + U (2.4g.), heated at 150°.160° for 1½ hours, treated with water and dilute ammonia.	Oxamide	Does not melt below 270°	Ammonium salt is also formed in this and the following cases. CO <sub>2</sub> is evolved.
Succinic acid	A (2.2g.) + U (2.4g.), heated as above. Imide extracted with acetone and purified from; benzene amide obtained by treating the mass with water.	Succinimide Succinamide	126° 212°	A better yield of the imide obtained by distilling the mixture.
Methylsuccinic acid.	A (2g.) + U (2.6g.), heated as above. Imide extracted with ether.	Pyrotartramide Pyrotartrimide	225° 66°	
Phthalic acid	A (1.7g.) + U (1.2g.), heated at 150°.160° for 2 hours, treated with water and dilute ammonia.	Phthalimide	233°	Yield 30%
Camphoric acid	Heated as above	Camphorimide	248°	Yield 40%
Quinolinic acid		Quinolimide	280°	Yield 35%

TABLE III.

*Reactions of Acid Anhydrides with Urea.*

(A = Anhydride; U = Urea).

Anhydride used.	Reaction and isolation.	Products formed.	M.p and mixed m p.	Remarks and analysis.
Methyl succinic anhydride.	A (1 mol.) + U (3 mols.), heated at 160° for one hour, extracted with acetone and purified with ether.	Pyrotartrimide	68°	CO <sub>2</sub> is freely evolved in all these cases.
Phthalic anhydride.	A (1.5 g.) + U (1.2 g.), heated at 160°-160° for 1 hour, treated with water and dilute ammonia.	Phthalimide	283°	Yield quantitative. The melting point is not raised by crystallisation from ether. Dunlop ( <i>loc. cit.</i> ) obtained a product melting at 227° by using smaller proportion of urea. It was probably impure phthalimide.
Camphoric anhydride.	Excess of urea used at 170° for 1 hour.	Camphorimide	248°	Yield almost quantitative.
Quinolinic anhydride.	Excess of urea used. Heated at 160° for 1 hour.	Quinolimide	230°	
Diphenic anhydride.	Heated as above with 3 mols. of urea.	Diphenimide	219°	

TABLE IV.  
*Reactions of Urea in Various Solvents.*

Reactants.	Alcohol (96 %).	Alcohol (50 %).	Water.	Acetic acid.	Glycerol.	Remarks.
Aniline	No action	Phenyl and diphenylurea	Phenyl and diphenylurea	Diphenylurea	Diphenylurea	Yields are poor except in acetic acid
Aniline hydrochloride	Diphenyl urea (trace)	Diphenylurea	Diphenylurea (trace at 80-85°)	"	Phenyl and diphenyl urea	Yields much greater than in the case of free base
<i>p</i> -Aminobenzoic acid	Carbamido derivative	Carbamido derivative	Carbamido derivative	Mixture of carbamido derivative and carbo-di- <i>p</i> -aminobenzoic acid	Ammonium salts of <i>p</i> -aminobenzoic acid and its carbamido derivative.	
Benzoic acid	No action	Ammonium salt (partial)	Ammonium salt	No action	Ammonium salt	
Phenylacetic acid	"	"	"	"	"	No amide formed in any case
<i>o</i> -Phthalic acid	"	"	"	Phthalimide	Ammonium salt	
Phthalic anhydride			"	"	Phthalimide	

The author is indebted to Dr. U. N. Brahmachari for the facilities given for these investigations.

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# Variation in the Amounts of Ammoniacal and Nitric Nitrogen in Rain Water of Different Countries and the Origin of Nitric Nitrogen in the Atmosphere

BY N. R. DHAR AND ATMA RAM.

It is well known that an appreciable quantity of nitrites and nitrates falls on the earth's surface with rain water. The following table indicates a few observations.

Place.	Wt. of nitric N per acre brought down by the annual rainfall.
Caracas, Venezuela .	7.87 lb.
St. Denis, Island of Re-union . .	9.437
Lieb Frauenberg, Alsace ...	0.5214
Rothamsted, England ...	1.83

The nitrites and nitrates present in rain water are derived from the nitric nitrogen occurring in the atmosphere. The nitric nitrogen present in the atmosphere exists either as the oxides of nitrogen or as ammonium nitrate and nitrite. These are washed down to the soil by the rain and form an important source of nitrogenous compounds for the nutrition of plants. What is the origin of this nitric nitrogen? It was believed that the oxides of nitrogen owe their origin to thunder storms in the upper air; nitrogen and oxygen combine to form oxides of nitrogen due to electric discharge. But thunder storms do not occur frequently. If the presence of the oxides of nitrogen is to be ascribed to thunder storms, they will be washed down to the earth by the rain which follows thunder storms and no oxides of nitrogen should be present in the atmosphere on ordinary days. But this is not the case. The amount of the oxides of nitrogen present in air on ordinary days is practically the same as that present on days when thunder storm occurs. There is no relation between the variation of the nitrite and nitrate content of the atmosphere and the incidence of thunder storms.

According to Moore (*J. Chem. Soc.*; 1921, 119, 1655), sunlight causes a slight union of nitrogen and oxygen in the air, resulting in the formation of oxides of nitrogen. Dhar and Sanyal (*J. Phys. Chem.*, 1925, 29, 926) have observed the formation of traces of nitrite when air freed from impurities is bubbled through conductivity water in presence of mercury vapour lamp light and in sunlight.

The photochemical combination of nitrogen and oxygen appears to contribute a small part of the total nitric nitrogen present in the atmosphere. Very recently Gopal Rao and Dhar (*Z. anorg. Chem.*, 1931, 199, 422) have advanced the view that the important source of nitrites and nitrates in the atmosphere, is the photo-oxidation of ammonia by air in presence of sunlight.

It is well known that ammonia occurs in the atmosphere to an appreciable extent. The ammonia is derived from the decomposition of nitrogenous organic matter, from the burning of coal, etc. The air of manufacturing towns appears to be more rich in ammonia than the air of rural districts; for the huge consumption of coal in industrial centres sets free large amounts of ammonia. Thus Smith found in England 0.97 mg. of ammonia per litre of rain in the country (2.502 lbs. per acre) and 5.14 mg. in the town (13.4 lbs. per acre); and in Scotland 0.53 mg. in the country (1.381 lb. per acre) and 3.81 mg. in towns (9.928 lbs. per acre). J. A. Barral estimated that Paris received annually 20.83 lbs. of ammonia per acre and A. Bineau showed that Lyons had 73.53 lbs. per acre. This ammonia is continuously undergoing oxidation to nitrite and nitrate by the oxygen of the air under the influence of ultraviolet rays from the sun.

From the theory of nitrification advanced from these laboratories, it is expected that the ratio of nitric to ammoniacal nitrogen in the rain water, available in tropical countries should be much greater than the ratio obtained in the rain water collected in temperate and cold climates. In order to test this point, we have undertaken a systematic analysis of rain water, as no satisfactory data on this question are available. The procedure adopted in the analysis of rain water was as follows:

The rain water was collected in large porcelain dishes placed on a tall stool in an open space. A definite volume of the freshly collected rain water, usually 800 c.c., was taken in a distilling flask and evaporated to 20 c.c. in presence of potassium hydroxide, so that the ammonia present in rain water in the free and

combined states was removed. The nitrite and nitrate of rain water now present as potassium salts were reduced by Devarda's alloy. The ammonia obtained by the reduction was caught in two small flasks containing dilute sulphuric acid. After complete reduction of the nitrates and nitrites, the contents of the two flasks were made up to 250 c.c. The amount of ammonia so obtained was estimated by the colorimetric method using the Duboseq type of colorimeter and Nessler's reagent. The amount of nitrogen present in the ammonia obtained by reduction represents the sum of the nitric and nitrous nitrogen present in rain water. From this, the nitrogen due to the nitrites was deducted. The nitrites were estimated separately by the colorimetric method applying the well known  $\alpha$ -naphthylamine sulphanilic acid test. The amount of ammonia present in rain water in the free and combined states can be easily found by the colorimetric method taking the original rain water and comparing it with a standard ammonium chloride solution. That the ammonia obtained by the reduction was not due to impurities present in the Devarda's alloy and the alkali, a blank experiment, using the same amount of alloy and alkali as used in the analysis of rain water was always performed with conductivity water, and the amount of ammonia so obtained, if at all, was always deducted from the actual amounts available after the reduction. In the blank experiment with conductivity water, the alloy and alkali were heated in a flask in two instalments for a total period of 8 hours in order to obtain comparable results. In order that all the nitrite and nitrate present in rain water be reduced, the reduction should be carried on at least twice and the total time required for the reduction was 8 hours. It is well known that the estimation of small amounts of nitrates present in a large volume of water is difficult because it is exceedingly tedious to reduce the nitrates completely on prolonged boiling with alkali and Devarda's alloy. In our experiments, we boiled the rain water after concentration with alkali and the alloy in a flask in two instalments for a total period of 8 hours, each time adding a fresh sample of the alkali and the alloy. We have observed that most of the samples of Devarda's alloy contain small amounts of ammonium compounds, nitrites and nitrates. Hence in all our experiments, the amounts of ammonia derived from the impurities in alloy were always taken into account. In this connection, the following observations of Thresh ("The examination of waters and water supplies." 1918, p.

295) will be of interest:—"In no other determination do results differ so widely. On more than one occasion, I have had to give an opinion upon water which had been submitted to various well known analysts. The other determinations recorded in the analyses have usually been concordant, but the nitric nitrogen had varied enormously. This has not been due to any change in the water, as in some cases the samples were taken at the same time. The difference appears to be due to the methods employed."

We are of the opinion, therefore, that the estimation of small quantities of nitrate present in rain water is likely to be vitiated if special precautions are not taken and it seems likely that the earlier results on the nitric nitrogen content of rain water obtained by some previous workers may not be quite correct.

The following are the experimental results:

Date.	Ammoniacal N mg./litre.	Nitric N mg./litre.	Ratio of nitric to ammoniacal N.
Aug. 21, 1932	0.20	0.50	2.5
Sept. 2, 1932	1.02	2.56	2.5
" 3, "	0.17	0.70	4.1
" 3, "	0.16	0.70	4.4
" 4, "	0.24	0.70	3.1
" 5, "	0.17	0.61	3.6
" 6, "	0.11	0.45	4.1
" 6, "	0.10	0.43	4.3
" 16, "	0.60	1.65	2.7
" 16, "	0.28	0.88	3.1
" 16, "	0.24	0.87	3.6
Oct. 23, "	0.37	0.81	2.2
" 23, "	0.36	0.86	2.4
Mean	0.31	0.90	3.3

The foregoing results show, that in all cases, the ratio of nitric to ammoniacal nitrogen is much greater than unity and the average is 3.3. It will be interesting to note that the ratio of the nitric nitrogen

to ammoniacal nitrogen in rain water collected after the end of a heavy shower is greater than in the water collected in the beginning of the shower. It is difficult to explain this observation and we are carrying on experiments in order to throw light on this problem.

Our experimental results are in agreement with our theory of nitrification in the atmosphere. We have observed that the rain water collected at Allahabad is generally slightly acidic probably due to the presence of free nitric and nitrous acids.

It will be interesting to compare our values with those obtained in colder countries. According to Lawes and Gilbert the average amount of total nitrogen in country rain water is about 0·7 parts in million parts of water, whilst our value is 1·21 in the same volume of rain water.

We are of opinion that in tropical countries, the ratio of nitric to ammoniacal nitrogen is higher than unity due to two reasons, (1) the increased photo-oxidation of ammonia and its compounds to nitrous and nitric acids under the action of sunlight; (2) the slow combination of nitrogen and oxygen forming oxides of nitrogen in presence of the ultra violet light of the sun.

In the following tables we have collected the amounts of ammoniacal, nitric and total nitrogen available in rain water at different places.

TABLE I.

*Non-industrial Places (Tropics).*

Place.	Latitude.	Ammoniacal N in lbs. per acre.	Nitric N in lbs. per acre.	Ratio $\frac{\text{nitric N}}{\text{ammon. N}}$	Total amount of N brought down by rain in lbs. per acre.
British Guiana	5°0 N	1·006	2·541	2·5	3·547
Venezuela	10°30 N	—	7·870	—	—
Barbados	13°10 N	1·000	2·443	2·42	3·452
Reunion	21 S	—	9·437	—	—
Allahabad	25°28 N	2·020	5·865	2·9	7·885
Mean	—	1·334	5·631	2·6	—

TABLE II.

*Non-industrial Places (Temperate.)*

Place.	Latitude.	Ammonia- cal N in lbs. per acre.	Nitric N in lbs. per acre.	Ratio nitric N ammoniacal N	Total amount of N brought down in lbs. per acre.
DehraDun	30°19 N	2·037	1·368	0·67	3·405
Kokstad	30°34 S	1·702	1·021	0·6	2·7·8
Mississippi	33 S	—	—	—	3·636
Grahams town	33°19 S	1·448	1·16	0·804	2·603
Kansas	33 N	2·63	1·06	0·4	3·69
New Zealand coast	40 S	0·6	0·8	1·33	1·4
Cornell Mt. Vernon	40°26 N	2·64	1·755	0·66	4·395
Alsace	48°3 N	—	0·521	—	—
Rothamsted	51°49 N	· 4	1·33	0·50	3·97
Iceland	64°40 N	0·802	0·263	0·328	1·065
Hebrides	56°50 N	0·313	0·289	0·93	0·600
Ottawa	59°3 N	2·99	1·755	0·59	4·745
Mean	—	1·436	1·02	0·72	2·686

TABLE III.

*Industrial Places.*

Place.	Latitude.	Ammonia- cal N in lbs. per acre.	Nitric N in lbs. per acre.	Ratio nitric N ammoniacal N	Total N brought down by rain in lbs per acre
TROPICS					
Cawnpore (India)	26°28 N	2·482	0·768	0·31	3·25
Pretoria (S. Africa)	25°25 S	6·587	1·083	0·16	7·67
Mean	—	4·534	0·925	0·235	5·46
TEMPERATE					
Oedar (S. Africa)	32°22 S	7·093	1·321	0·16	8·409
Utah (U. S. A.)	39°30 N	5·06	0·356	0·07	5·416
Paris	48°51 N	—	—	—	8·98
Gembloax (Belgium)	50°33 N	—	—	—	3·2
Göttingen	51°57 N	4·0	1·2	0·3	5·2
Mean	—	5·362	0·959	0·179	7·481

From the foregoing survey of results obtained in the analysis of rain water in different countries, it seems that the ratio of nitric to ammoniacal nitrogen is greater in tropical than in countries situated in the temperate and frigid zones.

Moreover, it appears that the total nitrogen which falls with rain water is also appreciably greater in tropical countries. This increased amount of nitrogen which is available in the rain water of tropical countries may be ascribed to the following reasons:

(i) The combination of nitrogen and oxygen present in the air in presence of ultraviolet light from the sun.

(ii) The increased ammonification of the nitrogenous compounds present in the soil due to light absorption.

In publications from these laboratories we have shown that not only nitrification in the soil but also ammonification is accelerated by sunlight. In tropical countries, the surface of the earth received more sunlight than in temperate and cold countries and naturally there should be more nitrification and ammonification. A part of the ammonia escapes into the air and this addition of ammonia to the atmosphere appears to be more prominent in tropical than in non-tropical climates, because the soils in tropical countries attain a much higher temperature than in non-tropical countries. We have carried on experiments with urea solutions mixed with soil and have observed that there is more ammonia formed from urea in sunlight than in the dark and an appreciable amount of ammonia formed from the urea escapes into the air. In this connection the following remarks of Miller (*Chem. Soc. Annual Reports*, 1918, p. 212) will be of interest: "We have evidence that the fairly heavy soil at Rothamsted loses ammonia for some weeks after the application of ammonium salts and it is possible that some soils are more or less continuously giving into the air small portions of the ammonia produced from organic residues. Some soils may be expected to lose more ammonia than is returned in the rain, whilst others may gain in this manner more than they lose." Consequently in tropical countries, the atmosphere is richer not only in nitrites and nitrates but it also contains more ammonia than in non-tropical centres free from large industries.

It is well known that in industrial areas, the atmosphere is rich in ammonia and its compounds because of the combustion of large quantities of coal and decomposition of organic matter and that is why the amount of ammonia in places like Paris

Gembloux (Belgium), Pretoria, Cedar (South Africa), Utah (U. S. A.), Gröningen, etc., is higher than in country districts free from big industries. It will be interesting to note also that the ammonia content of rain water collected at Cawnpore (India), which is an industrial town is greater than that of Allahabad and Dehradun, which are non-industrial places. It seems certain, however, that the ammonia content of rain water of non-industrial places in the temperate and frigid zones is appreciably less than in places situated in the tropics. Hence the total nitrogen which comes to the soil from the rain water in tropical countries is appreciably greater than in non-tropical places. Consequently, the following statements of Miller and Russel need modification: "No countenance is given to the general belief that the Indian rainfall is richer in nitrogen than that of England." "That great differences in climate do not coincide with material differences in the amounts of nitrogen brought down by the rains." (cf. Miller, *Chem. Soc. Annual Reports*, 1906, p. 269).

"It is evident from all these results that as a source of combined nitrogen, the rain is of no great importance to crops—an average of wheat or barley will contain eight times nitrogen." (cf. Miller, *Chem. Soc. Annual Reports*, 1913, p. 211).

"It is now recognised that the quantities of nitrogenous compounds present in rain water are too insignificant to exert any appreciable effect" (cf. Russel, *Chem. Soc. Annual Reports*, 1919, p. 182).

In poor tropical countries, artificial manures are not much in use and naturally the crops and plants have to depend for their nitrogen requirements upon the soil which is hardly manured artificially and thus the supply of combined nitrogen from the rain, which is more important in tropical countries than in non-tropical countries, appears to assume importance in tropical agriculture.

#### SUMMARY.

(1) Careful analysis of rain water at Allahabad shows that the average amount of ammoniacal nitrogen is 0.81 part in million parts of water and of nitric nitrogen is 0.9 part in the same volume of rain water.

(2) The ratio of nitric to ammoniacal nitrogen has been found to be 2.9,



(3) This high ratio is due to the increased photo-oxidation of the atmospheric ammonia and its compounds by the oxygen of the air in presence of the ultra-violet light of the sun and the photo-chemical combination of nitrogen and oxygen of the air in sunlight.

(4) From the summary of the analysis of rain water carried on in various other countries, it appears that the ratio of nitric to ammoniacal nitrogen is greater in tropical countries than in non-tropical ones.

(5) Moreover it also appears that the total nitrogen, which falls with rain water on the surface of the earth is appreciably greater in tropical countries than in non-tropical countries. This is likely to be due to the increased photochemical combination of nitrogen and oxygen in tropical sunlight and the increase of ammonification of the nitrogenous compounds present in the soil due to sunlight and the escape of ammonia produced in ammonification to the atmosphere.

(6) The amount of ammoniacal nitrogen in rain water of industrial centres can be high and seems to depend on the coal consumption and decomposition of organic matter.

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# Viscosity of Liquids, their Boiling Points and Critical Temperatures.

BY BALBHADRA PRASAD.

While working on the Andrade-Sheppard formula (*Nature*, 1930, 125, 309-499) for the viscosity of liquids,  $\log \eta = \alpha + \frac{\beta}{T}$ , where  $\eta$  represents viscosity,  $\alpha$  and  $\beta$  constants, and  $T$  absolute temperature, a remarkable relation was found between  $\beta$  and the boiling point of the liquid expressed on absolute scale. In all the liquids examined the ratio of  $\beta$  to the boiling point of the liquid was found to be approximately constant, the ratio always lying between 1.04 and 1.24. Since the boiling points of liquids on the absolute scale are about 0.6 times the critical temperature expressed on the same scale, it was expected that a similar relationship would be found between  $\beta$  and critical temperature of liquids. In many cases the critical temperatures of the liquids are not known. In cases where the critical temperatures are known, it is found that the ratio of  $\beta$  to the critical temperature is a better constant, the ratio varying only from 0.64 to 0.73 as the following table shows.

Liquid.	$\beta$ .	Boiling temp $T_B$ .	Critical temp $T_C$ .	$\beta/T_B$ .	$\beta/T_C$ .
Methyl iodide	330	315	528.5	1.05	0.64
Ethyl bromide	335	311	499.0	1.06	0.67
Ethyl iodide	358	345	554.0	1.04	0.65
Propyl chloride	362	319	494.0	1.10	0.73
Propyl bromide	380	344	—	1.10	—
Propyl iodide	409	375	—	1.09	—
isoPropyl chloride	372	310	—	1.20	—
isoPropyl bromide	390	338	—	1.17	—
isoPropyl iodide	411	362	—	1.13	—
isoButyl chloride	428	341	—	1.24	—

Liquid.	$\beta$ .	Boiling temp. $T_B$ .	Critical temp. $T_C$ .	$\beta/T_B$ .	$\beta/T_C$ .
isoButyl bromide	440	364	—	1.20	—
isoButyl iodide	461	393	—	1.20	—
Allyl chloride	351	316	—	1.10	—
Allyl bromide	373	344	—	1.09	—
Allyl iodide	414	375	—	1.10	—
Chlorobenzene	468	405	635.2	1.15	0.73
Bromobenzene	488	429	670.0	1.14	0.73
n-Pentane	328	309	470.2	1.09	0.70
n-Hexane	370	341	523.3	1.08	0.71

Andrade has given a brief outline of his theory of the viscosity of liquids (*Nature*, 1931, 128, 835). Therein he considers the liquid state of matter to be more akin to the solid state. However, a relationship between  $\beta$  and the critical temperature means a relationship between  $\beta$  and Van der Waal's constants "a" and "b" for imperfect gases and unassociated liquids. From this it is apparent that  $\beta$  depends on the Van der Waal's constants. It is quite likely that if we use a formula like Van der Waal's equation instead of the simple gas law in the derivation of the viscosity of gases, we might get an equation involving "a" and "b" which might be true both for gaseous and liquid viscosities.

All the data for the viscosity of liquids were taken from Landolt-Börnstein's Tables.  $\beta$  for the various liquids was calculated from the above data.

#### SUMMARY.

(1) It has been shown that  $\beta/T_B$  and  $\beta/T_C$  are constants where  $T_B$  and  $T_C$  are the boiling points and critical temperatures of the liquids on the absolute scale, and  $\beta$  a constant occurring in the formula connecting viscosity and absolute temperature;  $\log \mu = a + \beta/T$ .

(2) Doubt has been expressed regarding the similarity in the liquid and solid state of matter suggested by Andrade.

## **A New Method for the Separation of Lead from Zinc and their Subsequent Estimations.**

BY KISHORI MCHAN SIL.

It has been found by Das-Gupta, Roy and Sil (*J. Indian Chem. Soc.*, 1928, 5, 657) that hydrogen peroxide and ammonium hydroxide can effect a quantitative precipitation of lead even in presence of nitrates and acetates of ammonia and alkalis, provided that the concentration of the salt present does not exceed the limits stated therein.

With increasing amounts of ammonium nitrate in solutions of lead nitrate, the colour of the lead precipitate, found to be mixtures of lead peroxide and oxide in different proportions, varies gradually from orange to yellow. These precipitates, on being gently heated over a small flame or in a crucible bath (*i.e.*, placing the crucible containing the precipitate on an asbestos ring fitted inside a bigger crucible near its bottom and then heating the latter strongly), give a yellow residue which on analysis was found to be pure lead monoxide. This observation together with the quantitative precipitation of lead within certain concentrations of ammonium nitrate (4 g. per 100 c.c. solution) serves as a basis for the estimation of lead in presence of ammonium nitrate by hydrogen peroxide and ammonia. There was no action, however, of hydrogen peroxide and ammonia on zinc salts, specially zinc nitrate, in presence of an excess of ammonia, and therefore after precipitation of lead, zinc can be estimated by the usual method.

### **EXPERIMENTAL.**

To a solution of lead nitrate, dilute nitric acid (1 or 2 drops) was first added and the solution was considerably diluted and then 2 c.c. of 3% hydrogen peroxide and 2 c.c. of concentrated ammonia added for 0.1 g. of lead, taking care that the total volume was always above 100 c.c. The voluminous precipitate so obtained was then heated on a water-bath ( $\frac{1}{2}$ –1½ hr.; longer in presence of ammonium nitrate), when it was converted into the crystalline state.

The precipitate was then filtered, washed with hot water till the wash-water was free from nitrate, dried and then heated gently over a small flame or in a crucible bath (*vide supra*) when a yellow residue was left behind. The residue was analysed by first converting it into the nitrate and then into sulphate. The results are given in Table I.

TABLE I.

$\text{NH}_4\text{NO}_3$ Soln. (8%) added.	Wt. of residue.	Wt. of $\text{PbSO}_4$ from the residue.	% of lead in the residue.
5 c.c.	0.1050 g.	0.1427 g.	92.83
10	0.0991	0.1347	92.85
15	0.1258	0.1710	92.84
20	0.0952	0.1393	92.77
30	0.1144	0.1554	92.80
40	0.1131	0.1534	92.86
50	0.0470	0.0638	92.74
0	0.0848	0.1152	92.81
0	0.0990	0.1356	92.82
0	0.1123	0.1526	92.83

The above results show that the yellow residue is purely  $\text{PbO}$ , as the percentage of lead contained in it corresponds to the theoretical value 92.83.

*Estimation of Lead in presence of Ammonium Nitrate.*

Exactly 16.55 g of lead nitrate were dissolved in 500 c.c. of water. In this solution, as a check, lead was also estimated as  $\text{PbSO}_4$  and as  $\text{Pb}_2\text{O}_7, 8\text{H}_2\text{O}$ , which gave 0.1087 g. and 0.1082 g. of lead respectively in 5 c.c. of the solution; whereas from the weight of lead nitrate taken, lead present in 5 c.c. of the solution is 0.1085 g. or 0.1115 g. as  $\text{PbO}$ .

5 C.c. of this lead nitrate solution were taken and mixed with different amounts of ammonium nitrate solution. From the mixture lead is precipitated by hydrogen peroxide and ammonia and the precipitate was washed, dried and then converted into yellow  $\text{PbO}$  and weighed as such. (For particulars, *vide infra*. The results are given in Table II).

TABLE II.

Pb (NO<sub>3</sub>)<sub>2</sub> soln. = 5 c.c.    Wt. of PbO present = 0.1115 g.

NH <sub>4</sub> NO <sub>3</sub> soln. (8%) in c.c.	5	10	15	20	30	40	50
Wt. of PbO found in g.	0.1113	0.1113	0.1115	0.1117	0.1114	0.2118	0.1112

*Separation of Lead from Zinc and their Estimations.*

About 20.5 g. of zinc nitrate were dissolved in 500 c.c. of water. From this solution zinc was estimated as ZnNH<sub>4</sub>PO<sub>4</sub> and also as Zn<sub>3</sub>P<sub>2</sub>O<sub>7</sub> (*vide* Treadwell and Hall, Vol. II). 10 C.c. of the solution gave 0.2470 g. of ZnNH<sub>4</sub>PO<sub>4</sub> and 0.2111 g. of Zn<sub>3</sub>P<sub>2</sub>O<sub>7</sub>.

Measured volumes of lead and zinc nitrate solutions were mixed together and the total volume made up to 100 c.c. Lead was precipitated from this solution with requisite amount of hydrogen peroxide and excess of ammonia. The solution with the precipitate was then heated on a water-bath till the precipitate attained a crystalline condition. During the course of heating small amounts of concentrated ammonia were occasionally added to replenish the loss of ammonia due to evaporation, thus preventing the precipitation of any zinc. The crystalline lead precipitate was then filtered and washed by decantation with hot water containing ammonia for at least 8 or 4 times till the wash-water was free from zinc [tested by neutralising the wash-water with dilute nitric acid and then by adding (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> solution; if any white precipitate or turbidity appeared in this test, the turbid solution was added to the main bulk of the filtrate and the washing with hot ammoniacal water was carried further till the wash-water gave no such turbidity with (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>]. The filtrate was collected in a porcelain basin (of about 500 c.c. capacity) and allowed to evaporate on a water-bath after being made almost neutral (very slightly acidic) by adding nitric acid. The precipitate was finally washed on the filter first with warm water and then with a little alcohol which helped a quick drying of the precipitate. It was then dried in an air oven at temperature of 110°-120°.

The filter paper from which the precipitate had been removed was incinerated to ash in a weighed crucible; dilute nitric acid (a drop or two) was added and then the crucible was gently heated over

a small flame. The main bulk of the precipitate was then transferred to the crucible and heated over the tip of a small flame or in a crucible bath for complete conversion to PbO. An occasional stirring with a stout platinum wire was helpful to this conversion. The crucible with the PbO was then allowed to cool in a desiccator and then weighed.

From the filtrate in the basin, when it reached to a volume of about 150 c.c., zinc was precipitated as  $\text{ZnNH}_4\text{PO}_4$  following the standard method and estimated as such or as  $\text{Zn}_2\text{P}_2\text{O}_7$ .

In this way with mixtures of different proportions of lead and zinc nitrate solutions, several estimations are made, the results of which are given in Table III.

TABLE III.

Pb (NO <sub>3</sub> ) <sub>2</sub> solution.	Zn (NO <sub>3</sub> ) <sub>2</sub> solution.	H <sub>2</sub> O <sub>2</sub>	Conc.. NH <sub>4</sub> OH.	PbO found.	PbO present	ZnNH <sub>4</sub> PO <sub>4</sub> found.	ZnNH <sub>4</sub> PO <sub>4</sub> present
1 c.c.	50 c.c.	2 c.c.	10 c.c.	0.0224 g.	0.0223 g.	1.239 g	1.235 g.
50	1	20	20	1.119	1.115	0.0218	0.0247
5	50	2	12	0.1114	0.1115	1.238	1.235
25	50	10	12	0.5558	0.5575	1.233	1.235
40	5	16	16	0.8892	0.8920	0.1232	0.1235
10	10	4	10	0.224	0.223	0.248	0.247
10	5	4	6	0.223	0.223	0.1233	0.1235
5	10	2	10	0.1112	0.1115	0.2468	0.2470
5	5	2	6	0.1111	0.1115	0.1235	0.1235
1	1	2	6	0.0222	0.0223	0.0249	0.0247
15	15	6	10	0.3339	0.3345	0.3698	0.3705
2	2	2	6	0.0444	0.0446	0.0492	0.0494
2	40	2	10	0.0448	0.0446	0.9883	0.9880
5	25	2	10	0.1118	0.1115	0.6169	0.6175
						Zn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> found.	Zn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> present
2	20	2	10	0.0445	0.0446	0.4224	0.4222
10	10	4	10	0.2238	0.2230	0.2115	0.2111
40	5	16	16	0.8915	0.8920	0.1053	0.1055



It has also been studied that the precipitations of lead in presence of chlorine ions by hydrogen peroxide and ammonia are quantitative. But these lead precipitates on ignition do not form pure  $\text{PbO}$ . The nature of these lead precipitates and also that of their ignited products are under investigation, which will form the subject matter of a separate paper.

In conclusion, I am much thankful to Dr. D. N. Mallik, Principal, Carmichael College, Rangpur, for his kind permission and giving me every facility to conduct this work in the Chemical Laboratory of the College and also to Mr. P. N. Das-Gupta, M.Sc. of the Calcutta Soap Works and to Mr. J. C. Das, M.A., Professor of Chemistry, Carmichael College, Rangpur, for their occasional guidance and for the kindness they have shown in fully revising the paper.

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# On the Viscosity of Liquids and the Dependence of the Viscosity Constants on Constitutional Factors.

BY BALBHADRA PRASAD.

Porter (*Phil. Mag.*, 1912, **23**, 458) showed that the logarithm of the mobility (inverse of viscosity) of a liquid plotted against the logarithm of its vapour pressure at the same temperature gave a straight line. In other words,

$$\text{Log } \eta = m \log p + C_1 \quad \dots \quad (1)$$

where  $\eta$  represents viscosity,  $p$  vapour pressure and  $m$  and  $C_1$  two constants. From the integration of the Clausius-Clapeyron equation connecting  $Q$  (heat of evaporation),  $p$  (vapour pressure) and  $T$  (absolute temperature), it follows that

$$\log p = -\frac{Q}{RT} + C_2 \quad \dots \quad (2)$$

By combining equations (1) and (2) we get

$$\log \eta = a + \frac{\beta}{T} \quad \dots \quad (3)$$

where  $a$  and  $\beta$  are constants, an equation given in the form  $\frac{1}{\eta} = A e^{-\frac{Q}{RT}}$

by Dunn (*Trans. Faraday Soc.*, 1926, **22**, 401), in the form  $\eta = A e^{\frac{b}{T}}$

by Andrade (*Nature*, 1930, **125**, 300) and in the form  $\log \phi = -\frac{k}{T} + C$

where  $\phi = \frac{1}{\eta}$  by Sheppard (*Nature*, 1930, **125**, 480). Porter (*loc. cit.*) suggested

$$F(M) = f(\mu) = A + \frac{B}{T},$$

where  $\mu$  represents viscosity and  $M$  mobility ( $\frac{1}{\mu}$ ). It is surprising that Porter did not suggest that  $f(\mu) = \log \mu$ .

The relationship which Porter finds between  $T/T_0$  and  $T$  where  $T$  and  $T_0$  are the temperatures of the two liquids at which their viscosities are the same, can really be derived for unassociated liquids from  $\log \eta = a + \frac{\beta}{T}$ . By combining two such equations, it can be shown that

$$\frac{T}{T_0} = \frac{a - a_0}{\beta_0} \cdot T + \frac{\beta}{\beta_0}.$$

In other words  $T/T_0$  plotted against  $T$  will give a straight line as found by Porter (*loc. cit.*)

It is difficult to understand why  $T/T_0$  plotted against  $T$  should give a straight line in the cases where one or both of the liquids are associated. The formula which Andrade (*Nature*, 1930, 125, 582) suggests for the associated liquids has the form

$$\log \eta_0 = a_0 + \frac{\beta_0}{T_0 - \theta}.$$

If we combine this equation with  $\log \eta = a + \frac{\beta}{T}$ , the equation representing the viscosity of unassociated liquids, we get

$$\frac{T_0 - \theta}{T} = m (T_0 - \theta) + k \quad \dots \quad (4)$$

$$\frac{T_0}{T_0 - \theta} = m' T + k' \quad (5)$$

So if Andrade's formulæ be correct,  $T/T_0$  plotted against  $T$  should not give a straight line if one or both of the liquids are associated. Actually it does, as shown by Porter in case of mercury and the water (*loc. cit.*). Andrade (*loc. cit.*) also considers this to be an unfailing rule. Some more substances are being examined by the author to test the correctness or otherwise of this relationship.

The object of the present paper is two-fold: first to test the formula for non-associated liquids and secondly to see the extent to

which the constants  $\alpha$  and  $\beta$  depend on the constitution of the compounds. The following liquids have been examined: pentane, isopentane, hexane, isohexane, heptane, isohexane, octane, methyl iodide, ethyl iodide, propyl iodide, isopropyl iodide, butyl iodide, isobutyl iodide, allyl chloride, allyl bromide, allyl iodide, ethyl bromide, isopropyl chloride, isopropyl bromide, propyl chloride, propyl bromide, isobutyl chloride, isobutyl bromide, mono-chloro-benzene, and mono-

## EXPERIMENTAL.

*of the Formulae for the Viscosity of  
Liquid Liquids.*

In the following Tables  $\eta$  (observed),  $\eta$  (calculated) and the % difference between the calculated and observed results for the various liquids are given.

*n-Pentane.*

$$\alpha = 4.2600, \quad \beta = 328.$$

$t^\circ$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.
0	2634	2693	0.0
10	2624	2624	0.0
20	2395	2395	0.0
30	2200	2200	0.0

*isoPentane.*

$$\alpha = 4.1011, \quad \beta = 339.$$

$t^\circ$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.
0	2438	2438	0.0
10	2564	2563	0.0
20	2331	2330	0.0

*n-Hexane.*

$$\alpha = 4.2495, \quad \beta = 370.$$

$t^\circ$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.
0	4020	4025	0.1
10	3602	3605	0.1
20	3258	3253	0.2
30	2963	2955	0.3
40	2708	2701	0.3
50	2483	2482	0.0
60	2238	2294	0.3

*isoHexane.*

$$\alpha = 4.2358, \quad \beta = 366.$$

$t^\circ$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.
0	3760	3771	0.3
10	3381	3381	0.0
20	3061	3054	0.2
30	2791	2778	0.0
40	2541	2542	0.0
50	2331	2339	0.3
60	2161	2162	0.0

*Heptane.*

$$\alpha = 4.2336, \quad \beta = 406.$$

$t^{\circ}$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.	$t^{\circ}$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.
0	5236	5249	0.2	50	3105	3095	0.3
10	4653	4658	0.2	60	2841	2837	0.1
20	4163	4162	0.0	70	2617	2614	0.1
30	3754	3746	0.2	80	2413	2420	0.3
40	3410	3395	0.4	90	2239	2250	0.5

*isoHeptane.**Octane.*

$$\alpha = 4.2316.$$

$$\beta = 396.$$

$$\alpha = 4.1790.$$

$$\beta = 456.$$

$t^{\circ}$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.
0	4811	4811	0.0
10	4278	4268	0.2
20	3842	3830	0.3
30	3472	3456	0.5
40	3152	3139	0.4
50	2881	2868	0.4
60	2642	2635	0.3
70	2426	2433	0.3
80	2243	2254	0.5
90	2087	2101	0.7

$t^{\circ}$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.
0	7060	7068	0.1
10	6159	6169	0.1
20	4828	4830	0.3
30	4828	4830	0.0
40	4328	4324	0.1
50	3907	3897	0.3
60	3551	3535	0.5
70	3241	3224	0.5
80	2971	2957	0.5
90	2730	2724	0.2
100	2520	2521	0.0
110	2335	2342	0.3
120	2160	2184	1.1

\*

*Propyl chloride.**isoPropyl chloride.*

$$\alpha = 4.3190.$$

$$\beta = 362.$$

$$\alpha = 4.2480.$$

$$\beta = 372.$$

$t^{\circ}$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.
0	4416	4416	0.0
10	3963	3963	0.0
20	3539	3533	0.2
30	3264	3264	0.0
40	2990	2987	0.0

$t^{\circ}$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.
0	4080	4080	0.0
10	3646	3652	0.2
20	3292	3294	0.1
30	2993	2990	0.1

c

*isoButyl chloride.*

*Allyl chloride.*

$\alpha = 4\cdot2203.$ $\beta = 423.$				$\alpha = 4\cdot3290.$ $\beta = 351.$			
$t^{\circ}.$	$\eta(0) \times 10^6.$	$\eta(c) \times 10^6.$	% Diff.	$t^{\circ}$	$\eta(0) \times 10^6.$	$\eta(c) \times 10^6.$	% Diff.
0	5878	5884	0.1	0	4127	4127	0.0
10	5138	5138	0.0	10	3718	3717	0.0
20	4617	4612	0.1	20	3374	3372	0.1
30	4138	4134	0.1	30	3074	3075	0.1
40	3729	3731	0.1	40	2825	2827	0.1
50	3389	3388	0.0				
60	3090	3091	0.0				

*Chlorobenzene.*

*Bromobenzene.*

$\alpha = 4\cdot3278.$ $\beta = 468.$				$\alpha = 4\cdot4240.$ $\beta = 488.$			
$t^{\circ}.$	$\eta(0) \times 10^6.$	$\eta(c) \times 10^6.$	% Diff.	$t^{\circ}.$	$\eta(0) \times 10^6.$	$\eta(c) \times 10^6.$	% Diff.
10	9582	9582	0.0	10	14076	14076	0.0
15	8969	8969	0.0	15	13173	13135	0.4
20	8391	8416	0.3	20	12271	12289	0.1
25	7904	7912	0.1	25	11369	11525	1.5
30	7435	7452	0.2	30	10647	10825	1.7
40	6659	6637	0.3	40	9564	9619	0.8
50	5991	5981	0.2	50	8662	8609	0.6

*Ethyl bromide.*

*Propyl bromide.*

$\alpha = 4\cdot4601.$ $\beta = 335.$				$\alpha = 4\cdot4216.$ $\beta = 380.$			
$t^{\circ}.$	$\eta(0) \times 10^6.$	$\eta(c) \times 10^6.$	% Diff.	$t^{\circ}$	$\eta(0) \times 10^6.$	$\eta(c) \times 10^6.$	% Diff.
0	4866	4869	0.1	0	6509	6509	0.0
10	4407	4406	0.0	10	5815	5813	0.0
20	4020	4015	0.1	20	5241	5230	0.2
30	3678	3681	0.1	30	4748	4745	0.1
				40	4338	4322	0.4
				50	3966	3964	0.1
				60	3563	3553	0.0
				70	3374	3385	0.2

*Allyl bromide.*

$$\alpha = 4.4310. \quad \beta = 378.$$

$t^{\circ}$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.
0	6258	6241	0.3
10	5595	5597	0.0
20	5037	5047	0.2
30	4581	4581	0.0
40	4192	4184	0.2
50	3844	3844	0.0
60	3545	3551	0.2
70	3279	3292	0.4

*isoPropyl bromide.*

$$\alpha = 4.8582. \quad \beta = 890.$$

$t^{\circ}$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.
0	6106	6119	0.2
10	5448	5447	0.0
20	4894	4889	0.1
30	4431	4419	0.4
40	4028	4019	0.2
50	3680	3680	0.0

*isoButyl bromide.*

$$\alpha = 4.8062. \quad \beta = 440.$$

$t^{\circ}$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.	$t^{\circ}$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.
0	8277	8277	0.0	50	4695	4659	0.8
10	7257	7261	0.1	60	4265	4241	0.6
20	6433	6424	0.1	70	3902	3882	0.3
30	5749	5737	0.2	80	3573	3570	0.1
40	5179	5156	0.4	90	3260	3299	1.2

*Methyl iodide.*

$$\alpha = 4.5728. \quad \beta = 330.$$

$t^{\circ}$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.
0	6055	6049	0.1
10	5481	5481	0.0
20	5001	5001	0.0
30	4601	4591	0.2
40	4240	4255	0.4

*Ethyl iodide.*

$$\alpha = 4.5501. \quad \beta = 358.$$

$t^{\circ}$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.
0	7269	7269	0.0
10	6537	6583	0.1
20	5925	5916	0.2
30	5408	5391	0.2
40	4951	4955	0.1
50	4558	4555	0.1
60	4217	4219	0.0
70	3914	3925	0.3



*Propyl iodide.*

$$\alpha = \bar{4} \cdot 4755. \quad \beta = 402.$$

$t^{\circ}$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.
0	9485	9409	0.3
10	8892	8890	0.0
20	7482	7482	0.0
30	6689	6689	0.0
40	6087	6056	0.1
50	5527	5518	0.2
60	5065	5053	0.2
70	4662	4654	0.2
80	4304	4306	0.0
90	3987	4002	0.4
100	3714	3732	0.5

*isoPropyl iodide.*

$$\alpha = \bar{4} \cdot 4406, \quad \beta = 411.$$

$t^{\circ}$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.
0	8841	8832	0.1
10	7814	7814	0.0
20	6971	6972	0.0
30	6268	6272	0.1
40	5676	5672	0.1
50	5162	5166	0.1
60	4731	4730	0.0
70	4347	4350	0.1
80	4006	4027	0.5

*Butyl iodide.*

$$\alpha = \bar{4} \cdot 4414. \quad \beta = 445.$$

$t^{\circ}$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.
10	10320	10320	0.0
15	9701	9695	0.1
20	9166	9123	0.5
25	8635	8630	0.1
30	8189	8128	0.7
40	7298	7297	0.0
50	6762	6598	2.5(?)

*isoButyl iodide.*

$$\alpha = \bar{4} \cdot 3715. \quad \beta = 461,$$

$t^{\circ}$	$\eta(o) \times 10^6$	$\eta(c) \times 10^6$	% Diff.
0	11660	11490	1.5(?)
10	10010	10010	0.0
20	8753	8608	0.6
30	7774	7815	0.5
40	6970	6987	0.2
50	6291	6290	0.0
60	5712	5701	0.2
70	5218	5194	0.5
80	4785	4763	0.5
90	4397	4381	0.4
100	4064	4049	0.4
110	3770	3760	0.3
120	3496	3504	0.2

*Allyl iodide*

$$\bar{\alpha} = 4.4537. \quad \beta = 414.$$

<i>t</i> °.	$\eta(c) \times 10^6$	$\eta(c) \times 10^6$ .	% Diff.
0	9358	9337	0.2
10	8255	8252	0.0
20	7338	7355	0.0
30	6596	6617	0.3
40	5972	5975	0.1
50	5440	5437	0.1
60	4987	4977	0.2
70	4585	4578	0.2
80	4237	4231	0.1
90	3936	3927	0.3
100	3652	3661	0.3

All the observed values except those of chlorobenzene, bromobenzene and butyl iodide have been taken directly from the Bornstein-Landolt's table. The values for chloro- and bromobenzenes have been taken from John Castell-Evans Physico-Chemical Tables Vol. II, pages 588-589 and those for butyl iodide have been calculated from the values of relative viscosities given in Bornstein-Landolt's table.

It is evident from the tabulated values of observed and calculated viscosities that agreement between the calculated and observed values is quite good. In very few cases indeed the difference between the two values exceeds 0.5 %. All differences greater than 1% can safely be assigned to experimental errors (in case of unassociated liquids only).

*The Dependence of  $\alpha$  and  $\beta$  on Constitutional Factors.*

*$\alpha$  and  $\beta$  in the homologous series.*—The only regularity which is noted in the  $\bar{\alpha}$  values of compounds belonging to a homologous series is that  $\alpha$  goes on decreasing as more and more  $\text{CH}_2$  groups are added. The difference between the  $\alpha$  values of two compounds differing either by a  $\text{CH}_2$  or by  $\text{C}_2\text{H}_4$  group is far from constant. There is no regularity to be observed even if antilog  $\alpha$ , i. e., "A" values of Andrade are compared.

$\beta$  values show some regularity when the values of the two compounds differing by a  $C_2H_4$  group is compared. However, there is no regularity if the values of two compounds differing by  $CH_3$  group are compared. The difference between the  $\beta$  values of *n*-pentane and *n*-heptane is 78, *n*-hexane and *n*-octane 87, methyl iodide and propyl iodide 79, ethyl iodide and butyl iodide 87. These differences may be considered to be approximately constant.

*Effect of Replacing Chlorine by Bromine and Bromine by Iodine.*

In the following table  $\alpha$ ,  $\beta$  and  $A$  are given for a number of chlorides, bromides and iodides. The difference between  $\alpha$ ,  $\beta$  and  $A$  values of the chlorides and corresponding bromides and that between the bromides and corresponding iodides are indicated by  $\Delta\alpha$ ,  $\Delta\beta$  and  $\Delta A$

Liquid.	$\alpha$	$\Delta\alpha \times 10^4$	$A \times 10^7$	$\Delta A \times 10^7$	$\beta$ .	$\Delta\beta$ .
Chlorobenzene	1.3278		2227		468	
Bromobenzene	1.4210	962	2655	428	488	20
Ethyl bromide	1.4601		2885		335	
Ethyl iodide	1.5501	900	3.49	664	358	23
Propyl chloride	1.3190		2085		362	
Propyl bromide	1.4216	1026	2640	555	360	18
Propyl iodide	1.4755	539	2989	349	409	29
isoPropyl chloride	1.2480		1770		373	
isoPropyl bromide	1.3582	1102	2281	511	390	18
isoPropyl iodide	1.4406	824	2758	477	411	21
isoButyl chloride	1.2203		1661		423	
isoButyl bromide	1.3062	859	2024	363	440	17
isoButyl iodide	1.3705	643	2352	328	461	21
Allyl chloride	1.3299		2137		351	
Allyl bromide	1.4310	1011	2692	555	373	22
Allyl iodide	1.4537	227	2842	150	414	41

As is evident from the tabulated values that there is no relationship among the  $\alpha$  or  $A$  values of chlorides and corresponding bromides

and iodides. The difference between the  $\beta$  values of chlorides and bromides may be considered to be approximately constant. It varies from 17 to 22. The corresponding difference between the bromides and iodides varies from 21 to 41, and so cannot be considered constant even approximately.

#### SUMMARY.

- (1) The equation  $\log \eta = a + \frac{\beta}{T}$  connecting the viscosity of liquids with temperature is derived from the Porter's empirical relation between the vapour pressure and viscosity.
- (2) The viscosity of 25 liquids has been calculated from the above equation and compared with the experimental values.
- (3) No relationship between  $a$  and chemical constitution is found.
- (4) The difference between the  $\beta$  values of two compounds belonging to the same homologous series and differing in molecular weight by  $C_2H_4$  is about 80.
- (5) The difference between  $\beta$  values of chlorides and corresponding bromides is about 20.

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# **The Kinetics of Coagulation of Ceric Hydroxide Sol.**

BY M. V. NABAR AND MATA PRASAD.

Smoluchowski's equation (*Physikal. Z.*, 1916, 17, 557) for the kinetics of coagulation of a sol by electrolytes has been examined by several workers in the case of various sols. Mukherjee and Papacostantinou (*J. Chem. Soc.*, 1920, 117, 1563; see also Mukherjee and Majumdar, *J. Chem. Soc.*, 1924, 125, 785) studied the coagulation of the gold sol by different concentrations of several electrolytes spectrophotometrically and found that the ratios  $t_1 : t_2 : t_3 \dots$  where  $t_1, t_2, t_3$ , etc., are the times since mixing of the electrolytes of various concentrations required for the sol to reach the same stage of coalescence, are to a certain extent independent of the stage of coalescence. Desai (*Trans. Faraday Soc.*, 1928, 34, 181) also found in the case of the coagulation of thorium hydroxide sol that these ratios were fairly constant for certain concentrations of the coagulator.

The kinetics of the coagulation of the ceric hydroxide sol by electrolytes has been studied in the present investigation and samples of the sol dialysed and diluted to different extents have been used. The results obtained have been utilised for determining the conditions for observing the autocatalytic nature of the coagulation process.

## **EXPERIMENTAL.**

### *Preparation of the Sol.*

The concentration of the sol prepared by dialysis of a solution of ceric ammonium nitrate changes with the progress of the dialysis and therefore, the sol, used in this investigation was prepared by precipitating ceric hydroxide from a solution of ceric ammonium nitrate with excess of ammonium hydroxide. The

precipitate was washed free from ammonia, suspended in distilled water and boiled. At intervals of a few minutes, two or three c.c. of 2N HCl were added to it and the mixture was stirred vigorously.\* By adding fresh water to the mixture from time to time the boiling was continued until a fluorescent golden yellow sol of ceric hydroxide was obtained. This sol was then continuously dialysed for several days and the samples of the sol were taken out whenever required. The colloid content of the sol was estimated by coagulating the sol by ammonium chloride, washing the coagulum free from chloride and weighing it as  $\text{CeO}_2$ . The concentration of the sol was thus found to be 4.98 g.  $\text{CeO}_2$  per litre and it remained constant during the entire period of dialysis. The coagulation velocity was followed by the thermopile method used by Mukherjee and Majumdar (*loc. cit.*). The ceric hydroxide sol is coloured yellow and on coagulation becomes dirty white; hence the sample of the sol, used for the coagulation experiments, was placed in an optical cell which served as the colour filter to cut off the light that would be absorbed by the sol prior to coagulation.

A mixture of 5 c. c. of the sol and 5 c. c. of distilled water was placed in the optical cell and the observed deflection gave the initial reading before the coagulation sets in. Then 5 c. c. of the sol were mixed with a solution of sodium or magnesium chloride which was made up to 5 c. c. by the addition of distilled water, and the time of mixing was noted. The mixing of the sol with the electrolyte was done in the same way throughout the investigation. The mixture was then transferred to the cell and the deflections of the galvanometer were noted at different intervals. Such observations were taken with the original sol as also with the sols diluted twice and four times with distilled water (sols A, A/2 A/4). The results obtained are shown in Figs. 1-6, in which the deflection differences ( $D_i - D_t$ ), where  $D_i$  is the initial deflection and  $D_t$ , the deflection observed at time  $t$  after mixing the sol and the electrolyte, are plotted against  $t$ .

Curves 1—5 in Figures 1—3 refer to 450, 400, 350, 300 and 250 m. moles of NaCl per litre: curves 1—8 of Figures 4—6 refer to 8, 0.7 and 0.6 m. moles of NaCl.

FIG. 1.

Sol dialysed for 2 days (Sol A/2.)

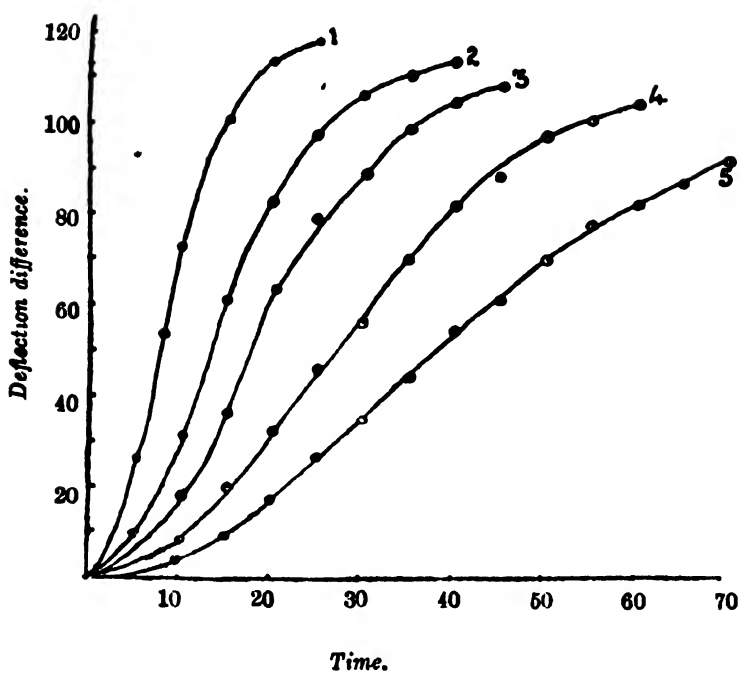


FIG. 2.

Sol A/2

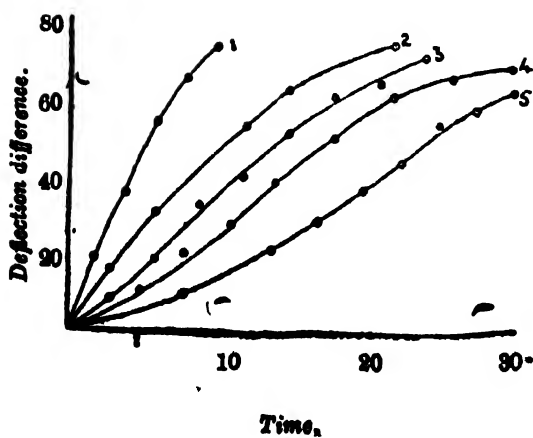


FIG. 3.

Sol A/4

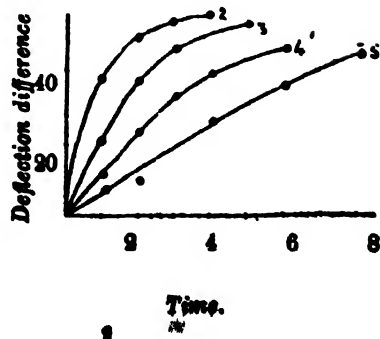


FIG. 4.  
Sol dialysed for 16 days.

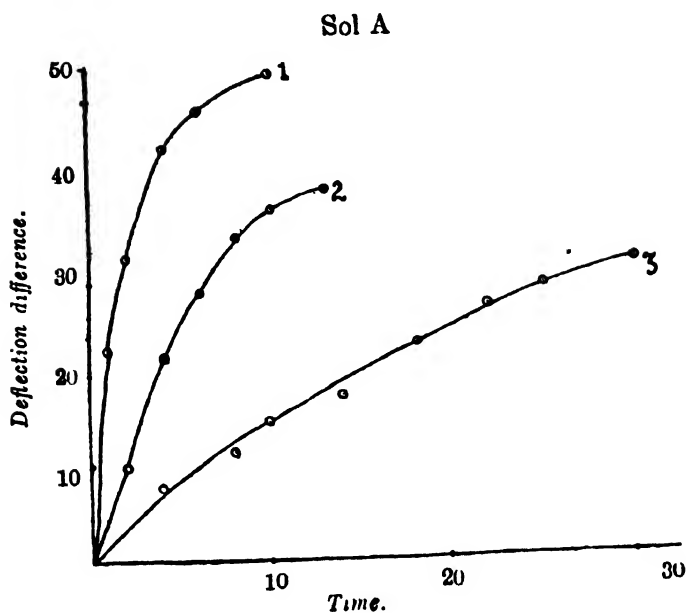


FIG. 5.

Sol A/2

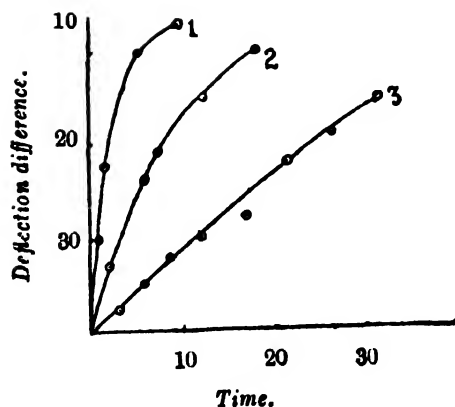
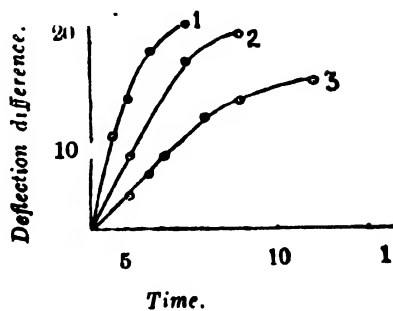


FIG. 6.

Sol A/4



## DISCUSSION.

The coagulation velocity curves for sols A dialysed for 2 days are 'S' shaped and shown in Fig. 1. Those dialysed for 6 and 10 days are also similar. The nature of the curves is changed when the sol is



further dialysed (*cf.* Fig. 4). This has been observed to be the case when either sodium or magnesium chloride is used as the coagulating electrolyte. The 'S' shaped nature of the curve is also found to disappear when the sol dialysed for different days is diluted (*cf.* Figs. 2, 3, 5, and 6). It, therefore, appears that the 'S' shaped nature of the coagulation velocity curves is intimately connected with (i) the amount of the stabilising ions and (ii) the concentration of the colloid. These results are in agreement with those obtained by Patel and Desai (*Trans. Faraday Soc.*, 1930, **26**, 106, 128) on thorium hydroxide sol.

The 'S' shaped nature of the coagulation velocity curves can be explained as done by Patel and Desai (*loc.cit.*) on the first and the second critical potential of Freundlich. But Desai and co-workers have found that with the progress of dialysis, the charge on the particles of the gold and thorium and ferric hydroxide sols first increases, reaches a maximum and then begins to decrease. In view of these results it is apparent that the potential of the colloid particles will for some days of the dialysis increase and will cause a slowing down in the rate of coagulation. The coagulation velocity curves should, therefore, become more and more 'S' shaped. The measurement of the charge on the colloid particles with the progress of dialysis should, therefore, be made before the above explanation can be expected.

The values of  $t$  for the same stage of coalescence have been read from the coagulation velocity curves for sols dialysed for 2, 6, 10 and 16 days and coagulated by different amounts of the two electrolytes. The values of the ratio are given in the tables I-IV. It will be seen from the results that the values of the ratios  $T_n/T$  are nearly constant for sol dialysed for two days and coagulated by solutions of sodium and magnesium chlorides of different concentrations. However the deviations of the values of  $T_n/T$  from the mean increase as the concentration of the electrolyte is decreased and the sol is further dialysed (*cf.* Tables for 6, 10 and 16 days). It appears that in addition to the concentration of the coagulator, the stage of coalescence of the particles may be another important factor which determines the applicability of Smoluchowski's equation.

TABLE I

<i>Sol (A) dialysed for 2 days.</i>						<i>Sol (A) dialysed for 6 days.</i>				
Deflection diff.	Conc. of NaCl in m. mols/litre.					Deflec- tion diff.	Conc. of NaCl in m. mols/litre.			
	450	400	350	300	250		62.5	56.25	50	43.75
	<i>T</i>	<i>T</i> <sub>1</sub> / <i>T</i>	<i>T</i> <sub>2</sub> / <i>T</i>	<i>T</i> <sub>3</sub> / <i>T</i>	<i>T</i> <sub>4</sub> / <i>T</i>		<i>T</i>	<i>T</i> <sub>1</sub> / <i>T</i>	<i>T</i> <sub>2</sub> / <i>T</i>	<i>T</i> <sub>3</sub> / <i>T</i>
16	1	1.9	2.7	3.9	5.4	4	1	1.3	2.5	5.8
24	1	1.8	2.4	3.5	4.9	8	1	1.4	2.1	4.5
32	1	1.8	2.3	3.5	4.8	16	1	1.4	2.3	4.5
40	1	1.8	2.3	3.5	4.9	24	1	1.5	2.4	3.9
48	1	1.8	2.3	3.6	5.1	28	1	1.5	2.5	3.8
						32	1	1.6	2.6	4.1
						40	1	1.7	2.9	4.5
						48	1	1.5	2.8	4.7

TABLE II.

<i>Sol (A) dialysed for 10 days.</i>					<i>Sol (A) dialysed for 16 days.</i>			
Deflection. diff.	Conc. of NaCl in m. mols/litre.				Deflection diff.	Conc. of NaCl in m. mols/litre.		
	13.75	12.5	11.25	10		8	7	6
	<i>T</i>	<i>T</i> <sub>1</sub> / <i>T</i>	<i>T</i> <sub>2</sub> / <i>T</i>	<i>T</i> <sub>3</sub> / <i>T</i>		<i>T</i>	<i>T</i> <sub>1</sub> / <i>T</i>	<i>T</i> <sub>2</sub> / <i>T</i>
4	1	1.2	3.2	6.5	8	1	1.9	7.7
8	1	2.5	4.6	8.3	12	1	2.1	9.1
12	1	2.1	4.2	7.2	16	1	2.5	10.6
16	1	2.0	4.0	6.7	20	1	2.9	11.7
20	1	1.9	3.7	6.4	24	1	3.3	12.8
24	1	1.9	3.6	6.1	28	1	3.4	13.9
28	1	1.9	3.6	6.2	32	1	3.6	14.7

TABLE III.

<i>Sol (A) dialysed for 2 days.</i>				<i>Sol (A) dialysed for 6 days.</i>			
Deflection diff.	Conc. of $\text{MgCl}_2$ in m. mols./litre.			Deflection diff.	Conc. of $\text{MgCl}_2$ in m. mols./litre.		
	175 <i>T</i>	150 <i>T</i> <sub>1</sub> / <i>T</i>	125 <i>T</i> <sub>2</sub> / <i>T</i>		31·25 <i>T</i>	28·125 <i>T</i> <sub>1</sub> / <i>T</i>	25·0 <i>T</i> <sub>2</sub> / <i>T</i>
16	1	1·7	2·6	4	1	1·9	3·9
24	1	1·8	2·5	8	1	1·7	3·2
32	1	1·7	2·4	16	1	1·7	2·7
40	1	1·7	2·5	24	1	1·7	2·7
48	1	1·7	2·6	32	1	1·7	2·7
56	1	1·8	2·6	40	1	1·6	2·6
64	1	1·8	2·6				
72	1	1·9	2·7				
80	1	1·9	2·8				

TABLE IV.

<i>Sol (A) dialysed for 10 days.</i>				<i>Sol (A) dialysed for 16 days.</i>			
Deflection diff.	Conc. of $\text{MgCl}_2$ in m. mols./litre.			Deflection diff.	Conc. of $\text{MgCl}_2$ in m. mols./litre.		
	7·5 <i>T</i>	6·25 <i>T</i> <sub>1</sub> / <i>T</i>	5·625 <i>T</i> <sub>2</sub> / <i>T</i>		4·0 <i>T</i>	3·5 <i>T</i> <sub>1</sub> / <i>T</i>	3·0 <i>T</i> <sub>2</sub> / <i>T</i>
4	1	2·3	8·0	4	1	2·0	6·0
8	1	2·6	7·3	8	1	2·0	7·0
12	1	2·6	6·3	12	1	1·9	7·3
16	1	2·6	5·6	16	1	2·0	8·3
20	1	2·7	5·5	20	1	2·1	8·2
24	1	2·7	5·2	24	1	2·3	9·5
28	1	2·7	5·1				
32	1	2·8	5·1				



## Presence of Formaldehyde in the Terrestrial and Solar Atmospheres.

BY N. R. DHAR AND ATMA RAM.

In a recent communication (*Nature*, 1932, 130, 313) we have reported that freshly collected rain water contains appreciable amounts of formaldehyde. In the months of June, July, August, and September, 1932, we analysed numerous samples of rain water and estimated quantitatively the amounts of formaldehyde present per litre of freshly collected rain water by the well known iodine method. We have observed that the amount of formaldehyde varies from 0.00015 g to 0.001 g. per litre of rain water. We have found that the quantity of formaldehyde present in a particular sample of rain water becomes exceedingly small, if it is collected after a very heavy shower. In order that appreciable amounts of formaldehyde may be detected in a sample of rain water, the rain water should be collected after some sunny days and it should be analysed immediately after collection.

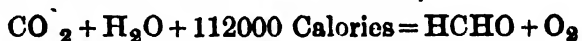
It is well known that carbonic acid and water vapour exist in the atmosphere and under the influence of ultraviolet light from the sun, they should combine and form formaldehyde and oxygen. Hence it seems probable that formaldehyde should be present in the atmosphere. If appreciable amounts of formaldehyde were present in the atmosphere, it should be partially washed down with rain water.

It is generally believed that hardly any radiation from the sun shorter than  $2900\text{\AA}$  is available on the earth's surface. Moreover, it is assumed that a very thin layer of ozone (3 mm. when reduced to 760 mm. pressure) formed in the atmosphere at higher altitudes, is capable of absorbing solar radiations shorter than  $2900\text{\AA}$ . This ozone is supposed to be formed by the absorption of shorter radiations by the oxygen of the atmosphere.

As a result of absorption measurements various physicists notably Fabry and Buisson (*Astrophys. J.*, 1921, 54, 297 ; Mecke, *Trans. Faraday Soc.*, 1931, 29, 375), Dobson (*Proc. Roy. Soc.*, 1930, A 129, 411) and others have concluded that the mean altitude of the ozone layer in the atmosphere is about 50 kilometers.

Our experimental observations on the existence of formaldehyde in rain water show that it is present in the upper layers of the atmosphere. We are of the opinion that this formaldehyde is formed in the atmosphere as a result of the photochemical combination of carbon dioxide and water vapour present in the atmosphere under action of ultraviolet rays from the sun. It will be interesting to note that Lob (*Z. Elektrochem.*, 1906, 12, 282) reported to have obtained only traces of formaldehyde on passing a silent electric discharge in moist carbon dioxide, but Lunt (*Proc. Roy. Soc.*, 1925, A 108, 172) is of opinion that  $\alpha$ -particles,  $\beta$ -rays and the corona discharge in carbon dioxide and water vapour do not cause the formation of formaldehyde or formic acid.

It is well known that the reaction,



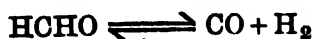
requires ultraviolet light of wave-length 2550 Å. In this connection it should be noted that we have shown in this laboratory that very seldom all the active rays are absorbed by an absorbing solution and hence it appears that all short ultraviolet rays coming from the sun will not be absorbed by the ozone layer present in the atmosphere. Some of the short-wave radiations are likely to pass through the ozone layer and decompose water into H and OH and these hydrogen atoms may reduce  $\text{CO}_2$  to formaldehyde. This reduction of carbon dioxide by atomic hydrogen appears to be accelerated by the action of short-wave radiations. The heat of dissociation of water into H and OH is 110,000 calories. In other words, the energy required in the formation of a gram mole of formaldehyde from carbon dioxide and water is practically the same as that required in the breaking of the H—OH link. As the energy requirements of both the reactions are the same, it appears that the chemical change involved in carbon assimilation is the photo-decomposition of water into H and OH. It appears that the function of chlorophyll and carotinoids present in leaves is that of a photo-sensitiser as well as that of a reducing agent helping the photo-reduction of carbonic acid. But the chief chemical change in photosynthesis appears to be the photolysis of water into H and OH by the absorption of energy of the sun.

In recent years the existence of free OH radical has been postulated by numerous workers. Thus Haber and his collaborators (*Z. Physik. Chem.*, 1928, 137, 268; *Z. Elektrochem.*, 1930, 36, 711), Hinshelwood (*Proc. Roy. Soc.*, 1928, A 118, 170) and Frankenburg (*Trans. Faraday Soc.*, 1931, 27, 481) have advanced the view

that OH radicals are formed in the combination of hydrogen and hydrocarbons with oxygen. Similarly the existence of OH has been assumed in the chain mechanism involved in the photochemical combination of chlorine and hydrogen in presence of moisture. Very recently, Franck and Haber (*Ber. Berl. Akad.*, 1931, 250), Haber and Wansbrough-Jones (*Z. Physikal. Chem.*, 1932, **18B**, 103), Farkas and Wansbrough-Jones (*ibid.*, 124) and others have suggested that not only in photochemical reactions taking place in aqueous solutions but also in catalytic and enzyme reactions OH radicals play an important rôle. It has been postulated that in many photochemical reactions taking place in aqueous solution, the primary change is the photolysis of water into H and OH. The secondary reactions are believed to take place between the atomic hydrogen and the OH radicals and the other substances present in the system.

It appears, therefore, that the mechanism of the formation of formaldehyde in the atmosphere is the same as that taking place in plants, the first stage being the photochemical decomposition of water into H and OH. Very recently Henri and Schou (*Z. Physik*, 1928, **49**, 744) and Herzberg (*Trans. Faraday Soc.*, 1931, **27**, 378) have measured the *ultraviolet* absorption of formaldehyde vapour and they are of opinion that the absorption spectra extend from 3700 Å to 2500 Å and that there are about 35 to 40 bands between 2500 Å and 3700 Å. The maximum absorption at 2935 Å is characteristic of aldehydes.

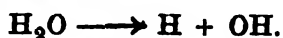
It is apparent, therefore, that not only ozone but also formaldehyde present in the atmosphere absorbs short rays of the solar radiations. Hence the absorption of solar radiations shorter than 2900 Å which has been so far attributed to the presence of ozone may be partially due to the formaldehyde present in the atmosphere. Formaldehyde in the atmosphere may also be decomposed under the influence of light. Recent experiments of Norrish and Kirkbride (*J. Chem. Soc.*, 1931, 1518) show that the main products of the photochemical decomposition of formaldehyde are carbon monoxide and hydrogen. It is evident, therefore, that the following equilibrium



may exist in the atmosphere. It is well known that the upper atmosphere is rich in hydrogen. Consequently due to the presence of hydrogen, the photo-decomposition of formaldehyde will be markedly

hindered and appreciable amounts of formaldehyde can exist in the atmosphere.

The following lines in the solar spectrum are attributed to the presence of OH group in the absorbing atmosphere of the sun. The OH lines in the solar spectrum may be due to the presence of OH formed from the photo-decomposition of water as depicted below :



Wave-length.	Intensity.	Wave-length.	Intensity.
3267.063	1	3147.448	1
3255.498	1N	3146.935	1
3238.554	-1	3146.599	1
3233.670	-1	3145.527	0
3229.884	0	3139.165	2
3226.447	-1	3137.897	-1
3218.076	-1	3136.891	1
3213.475	-1	3136.591	0
3210.725	-1	3134.338	1
3210.481	1	3131.447	0
3210.047	0	3130.568	1
3209.435	-1	3123.777	-1
3206.239	0	3125.522	0
3203.981	1	3127.093	-1
3202.698	0	3126.618	1
3202.258	-1	3124.919	2
3200.963	1	3123.260	1
3193.055	-1	3123.444	-1
3191.800	-1	3122.571	2
3189.318	0	3122.220	0
3188.060	1	3117.770	1
3181.991	3	3117.202	1
3181.642	-1	3117.088	-1
3160.492	0	3114.779	1
3179.967	-1	3114.629	-1
3177.681	1	3113.099	-1



Wave-length.	Intensity.	Wave-length.	Intensity.
3175·315	1	3106·023	2
3174·381	0	3105·678	1
3174·491	1	3104·350	-1
3172·938	1	3103·285	0
3169·862	0	3102·149	1
3169·617	0	3101·243	1
3168·956	1	3099·576	0 N
3167·178	1	3099·117	1
3166·336	0	3098·589	2
3164·549	0	3096·625	0
3161·902	0	3096·139	2
3158·522	0	3095·348	3
3157·502	1	3094·627	2
3156·846	0 N	3094·170	-1
3152·958	0	3093·609	-1
3152·458	-1	3092·104	1
3151·006	1	3091·372	1
		3091·214	1 N
3090·869	0	3077·028	0
3090·487	0	3075·136	0
3090·375	1	3074·386	1
3089·869	2	3072·183	0
3089·716	2	3071·116	1
3089·001	0	3070·498	1
3087·451	0	3070·381	-1
3087·346	1	3069·916	1
3086·230	0	3069·182	2
3085·207	2	3068·797	0
3084·898	1	3068·599	1
3084·056	-1	3068·282	1
3083·288	1	3067·658	1
3081·551	1	3064·956	1

Wave-length.	Intensity.	Wave-length.	Intensity
3081·248	2	3064·217	2
3080·246	0	3068·556	3

These lines have been obtained from the publication of St. John, Moore, Ware, Adams, Babcock (*Carnegie Institution of Washington*, 1928).

Moreover, hydrogen also escapes in the air from the occluded gases inside the earth and in marshy places. Also it can come to the atmosphere from the probable photo-decomposition of hydrocarbons like  $\text{CH}_4$ ,  $\text{C}_6\text{H}_6$  and of  $\text{H}_2\text{S}$ , etc. It is well known that ammonia exists in the earth's atmosphere. Moreover Fowler and Gregory (*Phil. Trans.*, 1919, **A218**, 351) have concluded from spectroscopic evidence that ammonia is present in the absorbing atmosphere of the sun. It is generally believed that cyanogen gas is also present in the solar atmosphere.

Recently Dhar (*Z. anorg. Chem.*, 1932, **206**, 270) has shown that several unidentified lines in the solar spectrum agree fairly well with the absorption spectra of formaldehyde vapour. Hence it has been concluded that formaldehyde may also form one of the ingredients present in the absorbing atmosphere of the sun. Moreover, it appears that free hydroxyl group is also present in the solar atmosphere.

What is the origin of these substances in the solar atmosphere? Very little is known about this point. In view of the various facts cited above, it is not at all surprising that formaldehyde is present both in the solar and the earth's atmosphere.

Further work in this line is in progress and we are trying to find out whether there is a relation between the incidence of thunderstorms and the amount of formaldehyde in the atmosphere.

#### SUMMARY.

1. Formaldehyde is present in rain water to the extent of 0·00015 g. to 0·001 g. per litre of freshly collected rain water.

2. It appears that the energy required in the formation of formdehyde from carbon dioxide and water vapour is the same as that required in the breaking of the H—OH link and the first stage in photosynthesis is the photo-decomposition of water into H and OH.

3. The formation of formaldehyde in the terrestrial atmosphere and in plants appears to be due to the reduction of carbon dioxide by the atomic hydrogen formed from the photolysis of water.

4. Several absorption lines in the solar spectrum are attributed to the existence of OH radical and formaldehyde in the absorbing atmosphere of the sun.

5. The decomposition of formaldehyde is hindered by the presence of hydrogen in the atmosphere.

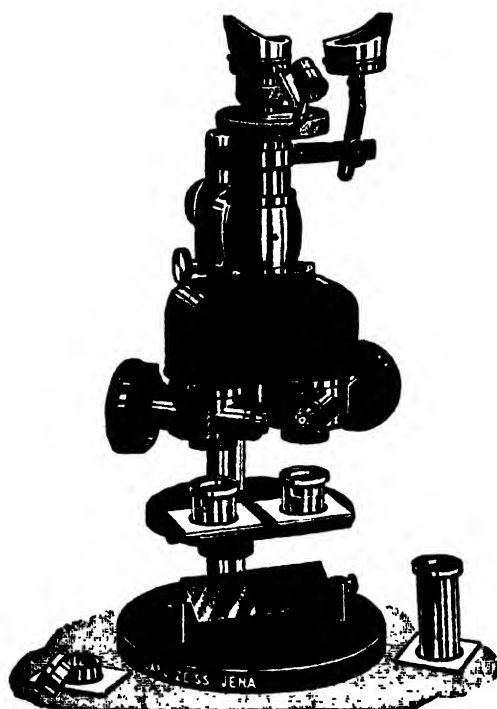
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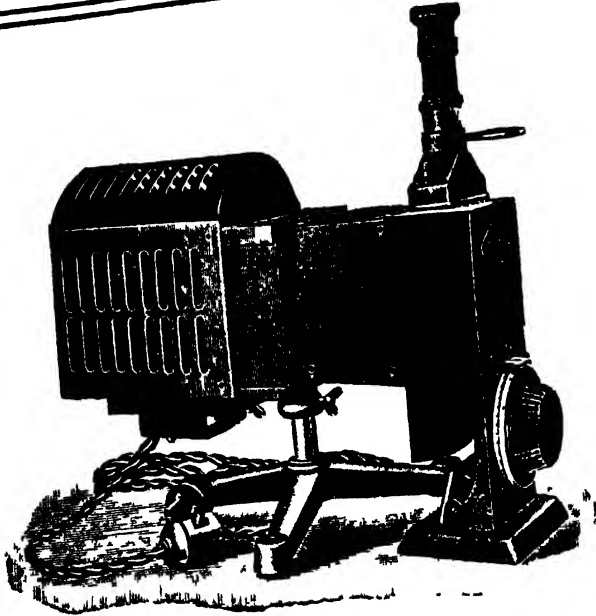
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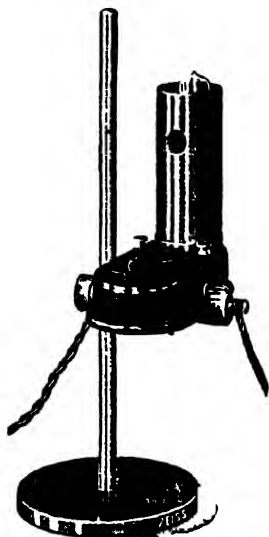


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# Studies on the Decomposition and Reactions of Urea.

## Part III. Reactions of Urea with Amines and Amino-acids.

BY JNANENDRA MOHON DAS-GUPTA

The reactions of urea with amines and amino acids, specially in aqueous solution, are of particular interest in connection with the much controverted constitution of "ureastibamine," obtained by the action of excess of urea on *p*-stibanilic acid in warm aqueous solution (Brahmachari, *J. Indian Med. Res.*, 1922, **10**, 492). Since it is a complex mixture, the constituents of which cannot be easily isolated and purified partly due to their gelatinous character, the results simply based on their analytical data are likely to be misleading. Other similar aromatic amino-acids, which are not unstable like *p*-stibanilic acid and the reaction products of which can be easily obtained in pure and crystalline states, have therefore been selected for comparing their actions on urea under similar conditions. In the case of aniline (or the hydrochloride), the reactions have been carried usually with an increasing proportion of urea, while Baeyer (*Annalen*, 1864, **131**, 252), Girard (*Ber.*, 1873, **6**, 444), Davis and Underwood (*J. Amer. Chem. Soc.*, 1922, **44**, 2595), Weith (*Ber.*, 1876, **9**, 821), Fleisher (*ibid.*, 1876, **3**, 998), Davis and Blanchard (*J. Amer. Chem. Soc.*, 1923, **45**, 1816) have carried the reactions with an increasing amount of the base (aniline). Different results have, therefore, been obtained with respect to the relative yields of the substituted ureas formed.

### EXPERIMENTAL.

*Aniline (or hydrochloride) and urea.*—The reaction products (phenyl and diphenylurea) are washed with water (20-30 c.c.) and separated by means of 50 % alcohol.

*p-Aminobenzoic acid and urea*.—A mixture of *p*-aminobenzoic acid (5 g.), urea (8 g.) and water (20 c.c.) was heated in a small flask on a water-bath for 2 hours. The amino-acid gradually dissolved and after about an hour a gelatinous precipitate separated out. The mixture was next diluted with water (20 c.c.) and filtered. The precipitate, after being thoroughly washed with water, was extracted with hot alcohol and filtered. The filtrate on evaporation yielded a white powder (2.2 g.) not melting below 275° and on analysis it was found to be carbamido-*p*-aminobenzoic acid. (Found: N, 15.23.  $C_8H_8O_3N_2$  requires N, 15.55 per cent).

The precipitate, insoluble in alcohol, was dissolved in alkali and reprecipitated with acid and the precipitate was washed with alcohol. The residue (about 0.3 g.) was found to be carbo-di-*p*-aminobenzoic acid. (Found: N, 9.1.  $C_{15}H_{12}O_5N_2$  requires N, 9.3 per cent).

The filtrate from the above precipitates, on acidification with dilute hydrochloric acid, yielded carbamido-*p*-aminobenzoic acid (1 g.) not melting below 270°. Evidently this was present in the solution as the ammonium salt, since the filtrate gave strong smell of ammonia on adding dilute alkali in the cold. The filtrate from the second precipitate was concentrated and then neutralised with dilute alkali and cooled, when a crystalline precipitate of *p*-aminobenzoic acid (0.8 g.), m. p. 116°, was obtained. It must also have been present in the solution as the ammonium salt.

The results obtained with various amines, amino-acids, etc are shown in the annexed tables.

## Reactions of Amines and Aminoacids with Urea.

Reactant.	Condition of experiment.	Products formed.	M. p. and mixed m. p.	Remarks.
Aniline	Aniline (3.8 g.) + urea (4 g., 2 mol.) heated at 150° for about an hour	Phenylurea Diphenylurea	147° 235°	Total yield, 2.6 g. Phenylurea, 2.2 g. (40%) Diphenylurea, 0.3 g. (7%)
Aniline hydrochloride	(a) Aniline hydrochloride (1.1 g.) + urea (4 g., 2 mol.) + water (20 c.c.) heated at 95-100° for 2½ hours (b) Aniline hydrochloride (2.6 g.) + urea (1.2 g.) heated at 150° for 1 hour	Phenylurea (0.7 g., 39%), Diphenylurea (0.1 g., 7%) Diphenylurea Phenylurea	147° 235° 147°	Filtrate from the precipitates yielded only a trace of diphenyl urea on refluxing for ½-1 hour.
8-Aminoquinoline dihydrochloride	(c) Aniline hydrochloride (2 g.) + urea (4 g., 2 mol.), heated at 150° for 1 hour Heated with equivalent quantities of urea in aqueous solution or in the dry state (15°)	Do Carbamido-8-aminoquinoline	147° 236°	Total yield, 70% Diphenylurea, 1.2 g. (59%) Phenylurea, 5 g. (18.3%) Total yield, 1.3 g. (60%) Phenylurea, 0.9 g. (43%) Diphenylurea, 0.3 g. (15%) No corresponding diquinolyl derivative formed
6-Aminocoumarin hydrochloride	Heated under the above conditions	Carbamido-6-aminocoumarin	245° (cf. Dey and Seshadri, <i>J. Indian Chem. Soc.</i> , 1931, 8, 298)	No disubstituted urea derivative formed

*Reactions of Amines and Amino-acids with Urea.*

Reactant.	Conditions of experiment.	Products formed.	M.p. and mixed m.p.	REMARKS.
<i>o</i> -Nitroaniline	Heated with excess of urea at 160° or 180°	No action	.....	Similar results obtained with <i>p</i> -nitroaniline, 4-methoxy-2-nitroaniline
<i>p</i> -Aminobenzoic acid	(a) Acid (5 g.), urea (8 g., 4 mol.) water (20 c.c.) heated on water-bath for 2 hrs. at about 93°	1 Carbamido- <i>p</i> -amino-benzoic acid (2.2 g.) 2. Do (1 g.) (as ammonium salt) 3. <i>p</i> -Aminobenzoic acid (0.8 g.) (as ammonium salt)	Not melting below 260°  Do 156	Carbo-di- <i>p</i> -amino benzoic acid formed only to a small extent (less than 0.3 g.)
	(b) The above reaction carried at 75-80° for 2 hours	Carbamido- <i>p</i> -amino-benzoic acid (ammonium salt)	Not melting below 260°	Yield, 2-3% The bulk of the amino acid remained unreacted.
	(c) Acid (1.3 g.), urea (0.6 g.) and water (5 c. c.), heated on water-bath for 2 hrs.	Carbamido- <i>p</i> -amino-benzoic acid (0.6 g.)	Do	Filtrate contained ammonium salt of the amino-acid.
<i>m</i> -Aminobenzoic acid	(a) Acid (5 g.), urea (6.7 g.) and water (15 c.c.), heated on water-bath for 2-2½ hrs.	1. Carbamido derivative (2.4 g.) 2. Do (1.2 g.) (ammonium salt) 3. <i>m</i> -Aminobenzoic acid	269° 269° 173°	

## Reactions of Amines and Amino-acids with Urea.

Reactant.	Condition of experiment	Products formed.	M.p. and mixed m.p.	Remarks.
<i>m</i> -Aminobenzoic acid	(b) Acid (1.5 g.), urea (1.5 g.) water (6.7 c.c.) heated as above	1. Carbamido derivative (0.8 g.) 2. Do. (0.15 g.) (ammonium salt)	163° 169°	
<i>o</i> -Aminobenzoic acid	Acid (5 g.), urea (8 g.), water (10-12 c.c.), heated on water-bath at 95°-100° for 2-2½ hours	1. Carbamido anthranilic acid (ammonium salt) 2. Ammonium anthranilate	153°	
<i>p</i> -Arsanilic acid	Acid (5 g.), urea (6 g.), water (10 c.c.) heated on water-bath for 3 hours	Ammonium- <i>p</i> -arsanilate		The ammonium salt was precipitated with absolute alcohol. No carbamido derivative formed

## DISCUSSION.

In the reaction of *p*-aminobenzoic acid with excess of urea, the main products formed are (1) carbamido-*p*-aminobenzoic acid, (2) ammonium salt of the same and (3) ammonium-*p*-aminobenzoate. A disubstituted urea derivative is not formed to any marked extent (also compare the reaction of aniline hydrochloride in presence of excess of urea). Since ureastibamine is formed from *p*-stibanilic acid and urea under similar conditions, it is unlikely that it should contain any appreciable quantity of *sym*-diphenylurea-4:4-distibinic acid (Gray, *Proc. Roy. Soc.*, 1931, B 108, 54). The reaction with arsenilic acid, to which *p*-stibanilic acid is very much allied, shows on the other hand, that no carbamido derivative is formed at all but simply the ammonium salt. It may be further noted that urea reacts very little with amines and amino-acids in aqueous solution at 75-80°. The following observations would throw further light on the constitution of the drug:

(i) An aqueous solution of ureastibamine is precipitated by an electrolyte, *e.g.*, NaCl or KI.

(ii) It gives diazo reaction. The presence of antimonie acid and other insoluble substances somewhat interferes with this test.

(iii) A concentrated aqueous solution of ureastibamine (2 g.) is heated with 5 % caustic soda solution at 70-75° for about 8 hours. An insoluble product (0.4 g.), consisting mainly of antimony oxide, gradually settles down. The filtrate, on acidification with dilute acetic acid, yields a voluminous precipitate (1.2 g.), which readily dissolves in dilute mineral acids (thus showing the absence of substituted urea derivatives). The above crude acid is purified by means of concentrated hydrochloric acid in the usual way and the pure stibanilic acid thus obtained is dried *in vacuo* over sulphuric acid. (Found: N, 5.0; Sb, 47.0.  $C_6H_5O_3NSb$  requires N, 5.3; Sb, 46.1 per cent). Carbamido-*p*-stibanilic acid does not yield *p*-stibanilic acid when heated with dilute alkali as above. Hence the formation of *p*-stibanilic acid in the above experiment from the decomposition of the corresponding carbamido derivative (Bramhachari and Das, *J. Indian Med. Res.*, 1924, 12, 423; Niyogi, *J. Indian Chem. Soc.*, 1928, 5, 758), if formed at all, is precluded. Probably *p*-aminophenylstibinic acid exists in a polymerised form in which the amino group is involved or may be that the latter group is in a loose state of combination with antimonie acid.



Summing all these facts, it appears that *p*-stibanilic acid is the principal constituent of the drug and as in *Neostibosan* it should be mainly responsible for its therapeutic value. It is present partly as the ammonium salt and partly in the free state (*cf.* observation *i*) together with some unhydrolysed acetyl-*p* stibanilic acid; the latter two colloidal substances are easily peptised in presence of antimonie acid and ammonia.

My thanks are due to Dr. U. N. Brahmachari for the facilities given for these investigations.

BRAHMACHARI RESEARCH  
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# The Kinetics of Coagulation of Titanium Dioxide Sol.

By S. M. MEHTA AND (MISS) OLIVE JOSEPH.

Smoluchowski (*Z. physikal. Chem.*, 1917, **92**, 129) proposed the following equation to represent the kinetics of rapid coagulation of a sol by electrolytes,

$$\Sigma_n = \frac{n_o}{1 + \frac{n_o}{kn_o t}} = \frac{n_o}{1 + \frac{t}{T}}$$

where  $n_o$  = the number of particles before the coagulation begins,  $K$  = velocity constant,  $t$  = the time since mixing of the electrolyte with the sol,  $T$  = specific coagulation time, given by the expression

$$T = \frac{1}{kn_o} - \frac{1}{4\pi Dn}$$

$r$  being the radius of the sphere of attraction and  $D$  the diffusion constant.

If  $\Sigma_n$ , which represents the same stage of coalescence, has a fixed value then

$$\frac{t}{T} = \frac{t_1}{T_1} = \frac{t_2}{T_2} \dots\dots\dots$$

or  $t:t_1:t_2\dots\dots\dots = T:T_1:T_2\dots\dots\dots$

where  $t, t_1, t_2$ , etc., are the times since mixing of the electrolytes of various concentration and  $T, T_1, T_2$ , etc., are the corresponding values of  $T$  for various mixtures. Since the values of  $T, T_1, T_2, \dots$  are fixed, their ratio is also fixed and should be independent of the stage of coalescence.

This theory has been verified by Zsigmondy (*Z. physikal. Chem.*, 1918, **92**, 600), Westgren and Reitstötter (*Z. physikal. Chem.*, 1918, **92**, 750) and by van Arkel (*Rec. trav. chim.*, 1920, **39**, 656).

For slow coagulation Smoluchowski has proposed the following expression :

$$T = \frac{1}{k_1 n_o} = \frac{1}{8\pi Dn_o}$$

He distinguishes rapid coagulation from the slow one in the sense that in the former all the collisions are fruitful in bringing about the coalescence of the micelles while in the latter only a small

fraction of this is effective. This expression for slow coagulation has been confirmed by Westgren (*Ark. Matem. Astron. Fys.*, 1918, 13, No. 14) and by Mukherjee and Majumdar (*J. Chem. Soc.*, 1924, 125, 794) up to a certain stage of coalescence.

It has been pointed out, however, by Miyazawa (*J. Chem. Soc. Japan*, 1912, 33, 1179), Ishizaka (*Z. physikal. Chem.*, 1913, 83, 97), Gann (*Koll-Chem Beih.*, 1916, 8, 65), Lottermoser (*Kolloid Z.*, 1914, 15, 145) and others that Smoluchowski's expression is not valid in the sensitive range of the electrolyte concentration. According to them, the coagulation is autocatalytic in nature and the coagulation velocity is best represented by the equation :

$$\frac{dx}{dt} = k(1+bx)(1-x).$$

Desai (*Trans. Faraday Soc.*, 1928, 24, 181) has studied the kinetics of coagulation of thorium hydroxide sol and has examined the validity of the Smoluchowski's equation and of the equation given above. Patel and Desai (*Trans. Faraday Soc.*, 1930, 26, 128) have studied the coagulation of thorium hydroxide sol during the progress of dialysis of the sol and have found that the purity and the concentration of the colloid are necessary factors in determining the autocatalytic nature of the coagulation process.

The coagulation of titanium dioxide sol by electrolytes during the progress of dialysis has been studied in the present investigation and an attempt has been made to examine the validity of Smoluchowski's equation. The method used by Mukherjee and Majumdar (*loc. cit.*) has been employed to measure the rate of coagulation. The titanium dioxide sol is not a coloured one, nor any change in colour takes place during coagulation and hence the objections raised by Desai (*loc. cit.*) against this method do not apply to this case.

#### EXPERIMENTAL.

*Preparation of the sol.*—Titanium dioxide sol was first prepared by Graham (*Phil. Trans.*, 1861, 151, 213), by adding hydrochloric acid solution to sodium titanate. Mazumdar (*J. Indian Chem. Soc.*, 1929, 6, 357) prepared the sol by adding titanium tetrachloride to distilled water, keeping the mixture at 18° and then dialysing it at room temperature. The sol prepared by both these methods was very unstable and coagulated before the chloride ions were removed.

In the present investigation the sol was prepared as follows: The titanium hydroxide was precipitated by adding ammonium hydroxide to titanium tetrachloride and was washed with hot water till free from ammonia. The suspension of the precipitate in a large volume of water was boiled and at certain intervals, 2N hydrochloric acid solution was added in small amounts until a clear sol was obtained. The total volume of the sol was kept constant by replacing the evaporated water from time to time. The sol thus prepared was transferred to a parchment bag which had been allowed to remain dipping in distilled water for 48 hours, and dialysed. During the dialysis no titanium was detected in the dialysate. The colloid content of the sol was found to be 1.2 g. of colloidal  $\text{TiO}_2$  per litre.

*Method of following the coagulation velocity.*—A parallel beam of light from a 25 c. p. lamp, enclosed in an asbestos box having a rectangular window, was made to fall on a rectangular optical glass cell filled with distilled water, whereby the heat rays were absorbed. It next fell on an optical glass cell containing the colloidal solution and finally on a thermopile which was connected to a sensitive galvanometer. The current feeding the lamp was maintained at a constant value. The deflection of the galvanometer with distilled water alone in the colloidal cell was 200 mm. and it remained constant throughout.

In a test tube 5 c.c. of the colloid were taken and in another a solution of the electrolyte, just sufficient to produce coagulation in about 30—35 minutes: the volume of the latter was made up to 5 c.c. by the addition of distilled water.

The mixture (electrolyte + water) was added to the colloid by gently pouring it down the sides of the test tube and the time of mixing the electrolyte with the colloid was noted. The same method of mixing the electrolyte with the colloid was used throughout. The mixture was then transferred to the colloid cell, the thermopile exposed to light at definite intervals and the deflections of the galvanometer were noted.

The relative distances between the various parts of the apparatus were kept constant throughout the series of experiments.

The titanium dioxide sol dialysed for 4, 10, 18, 24 and 82 days was studied using different concentrations of sodium chloride and magnesium chloride. The effect of dilution on the coagulation velocity was also investigated and for this purpose the sol is designated as A, A/2 and A/4.

The results obtained with sodium chloride and the sol dialysed for 4 days and those with magnesium chloride and the sol dialysed for 10 days are shown graphically in Figures 1 to 8. The deflection differences were obtained by subtracting the observed deflection from that given by 5 c. c. of the sol + 5 c. c. of water.

FIG. 1.

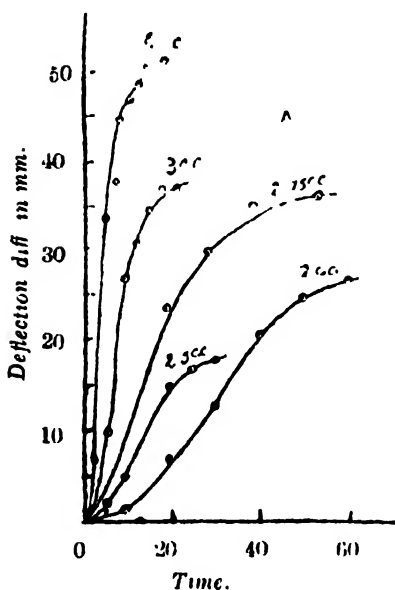


FIG. 2.

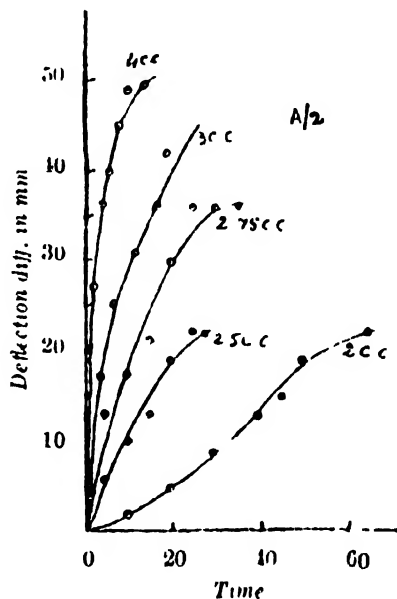


FIG. 3.

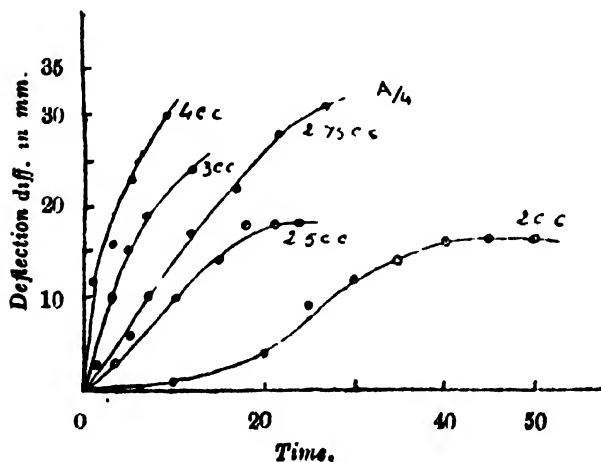


TABLE I

*TiO<sub>2</sub> Sol dialysed for 4 days.*

Electrolyte NaCl, 1N

Deflection. diff. in mm	Amount of the electrolyte in c c					Ratios				
	4	3	2.75	2.5	2	$T$	$T_1/T$	$T_2/T$	$T_3/T$	$T_4/T$
	$t$	$t_1$	$t_2$	$t$	$t_4$					
5	1	3	7	10	18	1	3	7	10	18
7	1	4	9	12	20	1	4	9	12	20
10	2	6	12	14	25	1	3	6	7	12.5
13	2	8	14	17	30	1	4	7	8.5	15
15	2	8	15	20	32	1	4	7.5	10	16
18	3	9	16	30	36	1	3	5.3	10	12
21	3	9	12	∞	40	1	3	4		13.3
24	4	9	19		46	1	2.25	4.75		11.5

TABLE II.

*TiO<sub>2</sub> Sol dialysed for 10 days.*

Electrolyte NaCl, 0.25N.

Deflection diff. in mm.	Amount of the electrolyte in c.c.				Ratios.			
	3	2.75	2.5	2	T	T <sub>1</sub> /T	T <sub>2</sub> /T	T <sub>3</sub> /T
	t	t <sub>1</sub>	t <sub>2</sub>	t <sub>3</sub>				
5	1	2	3	9	1	2	3	9
8	2	4	5	18	1	2	2.5	9
11	2	4	8	25	1	2	4	12.25
14	3	5	10	35	1	2	3.3	11.7
17	3	9	14	45	1	3	4.7	15
20	5	11	18	60	1	2.2	3.6	12
23	6	14	23	73	1	2.33	3.83	12
26	7	17	28	...	1	2.43	4	...
29	9	20	33	...	1	2.2	3.7	...
32	10	23	39	...	1	2.3	3.9	...



TABLE III.  
 TiO<sub>2</sub> Sol dialysed for 25 days  
 Electrolyte NaCl, 0.005N.

Deflection dif. in mm.	Amount of the electrolyte in c.c.				Ratios.			
	4 <i>t</i>	3 <i>t</i> <sub>1</sub>	2.75 <i>t</i> <sub>2</sub>	2.5 <i>t</i> <sub>3</sub>	<i>T</i>	<i>T</i> <sub>1</sub> / <i>T</i>	<i>T</i> <sub>2</sub> / <i>T</i>	<i>T</i> <sub>3</sub> / <i>T</i>
2	0.1	0.2	0.4	0.7	1	2	4	7
4	0.2	0.4	0.9	1.3	1	3	4.5	6.5
6	0.3	0.6	1.2	2.0	1	2	4	6.66
8	0.4	0.8	1.7	3.0	1	2	4.25	7.5
10	0.5	1.0	2.3		1	2	4.6	...
12	0.6	1.2	2.8		1	2	4.7	...
14	0.7	1.5	3.5	...	1	2.15	5	...
16	0.8	1.7	4.5	...	1	2.12	5.6	...
18	0.9	2.0	5.7	...	1	2.2	6.3	...
20	1	2.6	8	...	1	2.6	8	...

TABLE IV

*TiO<sub>2</sub> Sol dialysed for 10 days.*Electrolyte  $\text{MgCl}_2$ , 0.5N.

Deflection diff. in mm.	Amount of the electrolyte in c.c.						Ratios.		
	3'	2.75	2.5	2			$T_1/T$	$T_2/T$	$T_3/T$
	$t$	$t_1$	$t_2$	$t_3$			$T$		
5	0.8	2	6	10	1	1	2.5	7.5	12.5
8	1	3	9	14	1	1	3	9	14
11	1.7	4.5	11	17.5	1	1	2.6	6.5	10.3
14	3	6	13	20.5	1	1	2	4.3	6.8
17	4	7.5	14.5	24	1	1	1.9	3.73	6
20	5	9	16.5	27	1	1	1.8	3.2	5.4
23	6	10	18.5	31	1	1	1.66	3.08	5.2
26	7.5	11.5	20.5	35	1	1	1.5	2.7	4.7
29	9	13	23	40	1	1	1.44	2.6	4.4
32	10	14	25	50	1	1	1.45	2.5	

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TABLE V

 $\text{TiO}_2$  Sol dialysed for 18 days.Electrolyte  $\text{MgCl}_2$ , 0.06N.

Deflection diff. in mm.	Amount of the electrolyte in c.c.				Ratios		
	$t$	$t_1$	$t_2$	$t_3$	$T_1/T$	$T_2/T$	$T_3/T$
3		2.75	2.5	2			
2	0.5	1	2.5	5.5	2	5	11
5	1	2	6	12	2	3	12
8	1.1	3.25	1.5	19.5	1.4	5.6	11.5
11	2.5	1.75	1.9	24	1.3	5.2	11.6
14	3	6	16.5	—	2	5.5	—
17	3.75	8	20	—	2.5	5.3	—
20	4.75	10	24	—	2.1	5	—

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TABLE VI.

*TiO<sub>2</sub> Sol dialysed for 25 days.*Electrolyte MgCl<sub>2</sub>, 0.008 N.

Deflection diff. in mm.	Amount of the electrolyte in cc					Ratios.					
	4	3	2.75	2.5	2		$T$	$T_1/T$	$T_2/T$	$T_3/T$	$T_4/T$
t	t	t <sub>1</sub>	t <sub>2</sub>	t <sub>3</sub>	t <sub>4</sub>						
2	0.1	0.2	0.35	0.65	1.5	1	2	3.5	6	15	
4	0.2	0.3	0.7	1.3	3.5	1	1.5	3.5	6.5	17.5	
6	0.3	0.4	1.1	3.1	6	1	1.3	3.66	6.6	20	
8	0.4	0.55	1.6	3.2	10	1	1.25	4	8	25	
10	0.5	0.75	2	3	...	1	1.5	5	10	...	
12	0.6	0.9	2.55	6.2		1	1.5	4.1	10.3	...	
14	0.7	1.1	3.2	9	...	1	1.5	4.3	12.8	...	
16	0.8	1.4	4			1	1.6	5	...	...	
18	0.9	1.7	5		...	1	1.75	5.5	...	...	
20	1	2	5.3		..	1	1.9	5.3		...	

## DISCUSSION.

The values of  $t$ , for the same stage of coalescence, when different amounts of the electrolytes are added to the same volume of the sol, have been obtained from the coagulation velocity curves for "A" sols and the ratios  $\frac{T_1}{T}$ ,  $\frac{T_2}{T}$  .....etc., have been calculated for various stages of coalescence. The ratios obtained in the case of sodium chloride and the sol dialysed for 4, 10 and 25 days and those in the case of magnesium chloride and the sol dialysed for 10, 18 and 25 days are given in Tables I to VI for illustration.

It is observed that these ratios become more and more constant as the amount of the electrolyte is increased and as the sol gets purer. The percentage deviations of the ratios from the mean values are considerable for small amounts of electrolytes. This appears to indicate that Smoluchowski's equation is true only under restricted conditions.

It will be seen from Figs 1 to 3 that the coagulation velocity curves for "A" sol dialysed for 4 days are S-shaped and that the S-shaped tendency of the curves for the same amount of the electrolyte becomes less and less with an increase in the dilution of the sol. It is found that the S shaped nature of the curves disappears as the sol is dialysed further: the curves for sols dialysed for more than 18 days do not give S-shaped curves when they are coagulated by any concentration of sodium chloride.

In the case of sols coagulated by magnesium chloride similar results have been obtained.

It appears that the S-shaped nature of the coagulation velocity curves is intimately connected with the peptising ions present in the sols. Similar observations have been made by Patel and Desai (*loc. cit.*).

These results can be explained, as done by Patel and Desai (*loc. cit.*) in the case of thorium hydroxide sol, on the first and second critical potential of Freundlich. But the recent investigations by Desai and his collaborators (*Current Science*, 1982, 1, 38) on the measurement of charge on the colloid particles during the progress of dialysis of a sol, indicate that the charge does not decrease continuously as the dialysis is carried out for longer time. They find in the case of the thorium hydroxide sol that the charge

increases at first and then begins to decrease. This would mean that for the first few days of dialysis, the tendency of the sol should be to give rise to increased S-shape to the coagulation velocity curves. It is, therefore, necessary to carry out the charge measurements of titanium dioxide sol during the progress of dialysis and to study the coagulation velocity during the period when an increase in the charge on the colloid particles is taking place.

However, the results arrived at in this investigation confirm Patel and Desai's view that the concentration of a colloid is an important factor in determining the autocatalytic nature of the coagulation velocity curves.

#### SUMMARY.

1. The coagulation of titanium dioxide sol by sodium chloride and magnesium chloride has been followed by the thermopile method during the progress of dialysis of the sol.

2. The applicability of Smoluchowski's equation to the coagulation of the sol has been tested and it is found that it applies only for a limited range of the concentration of the coagulator.

3. The coagulation velocity curves (deflection differences against time) are S-shaped for sols dialysed up to 18 days: sols dialysed for longer time do not show the autocatalytic nature of the coagulation process.

4. The results of this investigation confirm the observations of Patel and Desai (*loc. cit.*) that (i) the S-shaped nature of the coagulation velocity curves is intimately connected with the peptising ions present and (ii) the concentration of the colloid is an important factor in determining the autocatalytic nature of the coagulation velocity curves.

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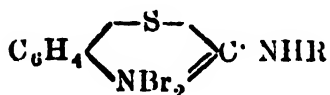
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# The Formation and Stability of Polybromide Derivatives of Heterocyclic Compounds. Part II. The Polybromide Ion Derivatives of Alkylaminobenzthiazoles obtained from *s*-Phenylalkylthiocarbamides and Bromine, and a Comparison of the Ease of Nuclear Substitution by Bromine in 1-Alkylaminobenzthiazolium and 1-Imino-2-alkyl-1:2-dihydrobenzthiazolium Ions.

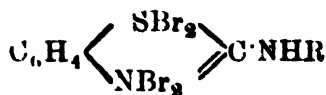
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AND SYED TUFAIL HUSAIN JAFFERY.

In view of the development of our knowledge of the chemistry of polybromide derivatives of heterocyclic compounds of the thiazole type in recent years, it appeared desirable to re-examine some of the earlier experiments on the bromination of *s*-phenylalkylthiocarbamides in chloroform.

The interaction of *s*-phenylalkylthiocarbamides with bromine was first examined some years ago in an investigation having for its main object the study of the relation between tautomeric mobility and unsaturation in semi-cyclic symmetrical triad systems (Hunter, *J. Chem. Soc.*, 1926, 1385, 2951). It was observed that certain phenylalkylthiocarbamides gave rise to what appeared to be dibromides and tetrabromides of the corresponding alkylaminobenzthiazoles, to which the formulæ (I) and (II) were assigned.



(I)



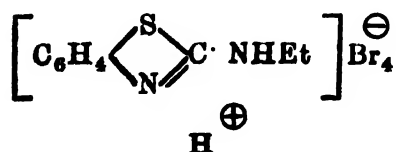
(II)

Owing to an erroneous theory of the mechanism of the reaction (Hunter and Soyka, *J. Chem. Soc.*, 1926, 2058), it was at this time assumed that bromo addition compounds of 1-aminobenzthiazoles containing an even number of bromine atoms labile towards sulphurous acid, obtained from arylthiocarbamides, were true bromides

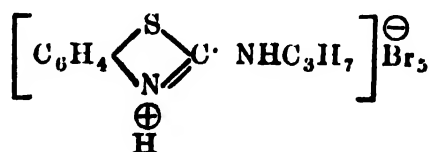
(*cf.* Hegershoff, *Ber.*, 1908, 36, 3121) of the type of 1-phenylbenzthiazole tetrabromide (Bogert and Abrahamson, *J. Amer. Chem. Soc.*, 1922, 44, 826; Hunter, *J. Chem. Soc.*, 1926, 537). The possibility that such compounds might be hydroperbromides was unfortunately never entertained, mainly on account of the fact that their formulation on such a basis, would have necessitated the assumption of "odd valency" structures. Later investigations, however, have shown that the bromo-addition compounds obtained by thiazole cyclisation of arylthiocarbamides are invariably *hydroperbromides* (Hunter, *J. Chem. Soc.*, 1930, 125; Dyson, Hunter, Jones and Styles, *J. Indian Chem. Soc.*, 1931, 8, 147), produced by the interaction of the hydrobromides of the thiazole bases initially formed and bromine. It has furthermore been shown that the nuclear nitrogen atom of the benzthiazole complex is the *centre* of unsaturation of the molecule, and that the sulphur atom of the heterocyclic ring resembles that of thiophen in its inertness towards ordinary reagents; due presumably to the fact that its labile electrons are called upon to complete the sextuple group on which the aromatic character of such heterocyclic systems may be assumed to depend (Armit and Robinson, *J. Chem. Soc.*, 1925, 127, 164, Goss and Inghold, *ibid.*, 1928, 1268; Hunter, *loc. cit.*). Formulae of the type (I) and (II) are therefore clearly erroneous, and since the technique in handling unstable bromo-addition compounds has been considerably improved in recent years the bromination of a number of *s*-phenylalkylthiocarbamides has been carefully re-investigated.

Treatment of a solution of *s*-phenylethylthiocarbamide in chloroform with excess of bromine gave rise to a well-defined *hydro-tetrabromide* of 1-ethylaminobenzthiazole, which was also prepared from the *hydrobromide* of the ethylaminobenzthiazole and bromine (*cf.* Hunter, *J. Chem. Soc.*, 1930, 134). This compound probably

has the constitution (III), containing a  $\text{Br}_4^\ominus$  ion, whose production involves the operation of a lone singlet linkage (*cf.* Dyson, Hunter, Jones and Styles, *loc. cit.*; Hunter, *Chem. Ind.*, 1932, 939).



(III)



(IV)



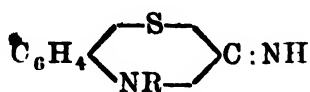
Bromination of *s*-phenyl-*n*-propylthiocarbamide in the presence of excess of the halogen, however, yielded an unstable *hydropentabromide* of 1-*n*-propylaminobenzthiazole to which the formula (IV) is assigned on the grounds of analogy with Roozeboom's ammonium pentabromide (*Ber.*, 1881, 14, 2398), which readily lost bromine giving a more stable *hydrotribromide* of the propylaminobenzthiazole. This was also obtained by carrying out the reaction in the presence of a lower concentration of the halogen, and it therefore appears probable that the 'tetrabromide' of 1-*n*-propylaminobenzthiazole, isolated under somewhat indefinite conditions in the earlier investigation (*loc. cit.*), consisted of a partially decomposed specimen of the *hydropentabromide* of the base.

Attempts to prepare bromo-addition compounds of 1-*isobutyl*-aminobenzthiazole and 1-*isoamyl*aminobenzthiazole of a higher order than *hydrotribromides* proved unsuccessful, the products of bromination of *s*-phenyl*isobutyl*thiocarbamide and *s*-phenyl*isoamyl*thiocarbamide being tenacious gums which crystallised with difficulty on being kept in *vacuo* over potassium hydroxide, giving the *hydrotribromides* of the corresponding alkylaminobenzthiazoles described in the earlier investigation.

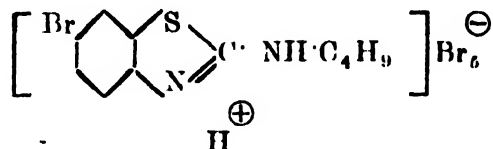
*s*-Phenyl-*n* hexylthiocarbamide, however, behaved similarly to the propylthiocarbamide and gave rise to an unstable *hydropentabromide* of 1-*n*-hexylaminobenzthiazole, which lost bromine on exposure to air or on keeping in a desiccator over potassium hydroxide.

A very definite contrast between the properties of the *hydropentabromide* of the 1-alkylaminobenzthiazoles and those derived from 1-imino 2-alkyl-1:2-dihydrobenzthiazoles (V) is provided by the respective tendencies of the compounds towards nuclear substitution. Thus, the *hydropentabromides* of the alkylaminobenzthiazoles undergo appreciable nuclear substitution by bromine under the ordinary conditions of iodometric titration of labile bromine in chloroform, whereas the bromo-addition compounds of iminoalkyldihydrobenzthiazoles give quantitative values for labile bromine (Hunter, *J. Chem. Soc.*, 1930, 139). Furthermore, the bromo-addition compounds of the alkylaminobenzthiazole series, such as the *hydrotetrabromide* of 1-ethylaminobenzthiazole, undergo nuclear substitution on being boiled in aqueous alcoholic solution, whilst the *hydropentabromides* of iminoalkyldihydrobenzthiazoles, in so far as they have been studied,

merely yield hydrobromides of the unsubstituted dihydrobenzthiazole bases under such conditions (*loc. cit.*).



(V)



(VI)

This difference in behaviour towards hydroxylic solvents is evidently attributable to the higher reactivity of the *para* position to the ring nitrogen atom in the thiazolium ion of the aromatic heterocyclic base towards bromine or hypobromous acid formed by decomposition of the polybromide complex in aqueous hydroxylic solvents.

The 1-alkylaminobenzthiazoles behave similarly to the iminoalkyl-dihydrobenzthiazoles on bromination in chloroform, and undergo nuclear substitution with the production of hydroperbromides of the corresponding 5-bromo-1-alkylaminobenzthiazoles. Thus, the *iso*-butylamino base on treatment with excess of bromine, yields a *hydro-pentabromide* (VI) whose constitution follows from its reduction by sulphurous acid to 5-bromo-1-*isobutyl*aminobenzthiazole, identical with that obtained from the thiazole cyclisation of *s-p*-bromophenyl-*isobutyl*thiocarbamide (Hunter and Soyka, *loc. cit.*).

#### EXPERIMENTAL

*s*-Phenylethylthiocarbamide was prepared by treating a solution of phenylthiocarbimide in absolute alcohol with a 20 to 30 % excess of a 33 % solution of ethylamine in water, and had m.p. 99–100° after recrystallisation (Weith, *Ber.*, 1875, 8, 1524).

**1-Ethylaminobenzthiazole hydrotetrabromide (III).** (i) *Bromination of s-phenylethylthiocarbamide.*—Bromine (1 c.c. in 2 c.c. of chloroform) was added to a solution of *s*-phenylethylthiocarbamide in chloroform (1 g. in 7 c.c.) in a Geissler flask, and the mixture was heated on a steam bath under reflux for 2 to 3 minutes and thereafter cooled in ice. The *hydrotetrabromide* crystallised in glistening orange-red needles which were collected on porous earthenware and dried in a vacuum over potassium hydroxide, anhydrous

calcium chloride, and paraffin wax for 5 to 10 minutes. After being crushed on fresh porous tile and again dried in a vacuum for a further 5 minutes, the crystals had m.p. 80–82° (softening and sintering at 70–74°). [Found: Br (total), 64.55; Br (labile), 43.8.  $C_9H_{10}N_2S.HBr(Br_3)$  requires Br (total), 64.15; Br (labile), 48.1 per cent]. The hydrotetrabromide dissolved in sulphurous acid giving a colourless solution which yielded 1 ethylaminobenzthiazole on basification with ammonia, which had m.p. 93–94° after recrystallisation from alcohol and drying in a vacuum (previously recorded as m.p. 87–88°)

(ii) *Synthesis from 1-ethylaminobenzthiazole hydrobromide and bromine*—The hydrobromide of 1-ethylaminobenzthiazole, obtained by treating a hot solution of the ethylamino base (1.5 g.) in absolute alcohol (9 c.c.) with 66 per cent hydrobromic acid (2 c.c.) and allowing the resulting solution to cool, crystallised in soft flakes consisting of small needles, m.p. 219–20° (Found Br, 30.7.  $C_9H_{10}N_2S.HBr$  requires Br 30.9 per cent). A warm suspension of this salt (1 g.) in chloroform (8 c.c.) was treated with bromine (0.8 c.c. in 1 c.c. of the same solvent), and the resulting clear red solution was cooled in the ice when the hydrotetrabromide separated in glistening orange red plates, m.p. 90°. [Found: Br (total), 64.0; Br (labile), 42.6 per cent].

*Decomposition of 1-ethylaminobenzthiazole hydrotetrabromide by alcohol and the Isolation of 5-Bromo-1-ethylaminobenzthiazole*—A solution of the bromo addition compound in alcohol was boiled, diluted with water and concentrated on a water-bath when acetaldehyde was evolved. The hydrobromide obtained in this way formed white flaky crystals which had m.p. 240–42° (sintering at 237–40°). It was decomposed with ammonia and the product was crystallised from alcohol when impure 5-bromo-1-ethylaminobenzthiazole was obtained which had m.p. 140°, and m.p. 146–48° when mixed with an authentic specimen prepared from *sp* bromophenyl-ethylthiocarbamide.

*1-n-Propylaminobenzthiazole hydro-pentabromide (IV)*.—A solution of *s*-phenyl-*n*-propylthiocarbamide (Hecht, *Ber.*, 1890, 23, 286) (0.7 g.) in chloroform (4 c.c.) was treated with bromine (0.9 c.c. in 0.9 c.c. of chloroform) and the mixture was heated on a water-bath under reflux for 2 minutes, and the solution was transferred to a dry crystallising basin and concentrated in a vacuum. The hydro-pentabromide crystallised in small vermilion crystals which were

collected on porous earthenware, dried in a vacuum over potassium hydroxide, anhydrous calcium chloride and paraffin wax for 2 minutes, transferred to fresh porous earthenware and again dried in a vacuum for a period of 5 to 10 minutes. This compound was highly unstable and showed signs of decomposition into the yellow-orange hydrotribromide on being exposed to moist air for a few minutes. It had m.p. 57-59° (clear red liquid at 60°). [Found: Br (total), 66.3; Br (labile), 52.6.  $C_{10}H_{12}N_2S \cdot HBr$  ( $Br_4$ ) requires Br (total), 67.6; Br (labile), 54.1 per cent]. On keeping in a desiccator over potassium hydroxide for 24 hours, it lost bromine yielding the yellow-orange hydrotribromide, and on reduction with sulphurous acid it gave 1-*n*-propylaminobenzthiazole, m.p. 68° (Hunter, *loc. cit.*).

*1-n-Propylaminobenzthiazole hydrotribromide*.—A solution of the phenylpropylthiocarbamide (1 g.) in chloroform (8 c.c.) was treated with bromine (1 c.c. in 1 c.c. of the same solvent) and the mixture was heated for 2 minutes and thereafter concentrated under reduced pressure at laboratory temperature. The yellow-orange crystals obtained in this way had m.p. 57° after being crushed on porous earthenware and dried in a vacuum. [Found: Br (total), 55.6; Br (labile), 36.4.  $C_{10}H_{12}N_2S \cdot HBr$  ( $Br_2$ ) requires Br (total), 55.4; Br (labile), 36.6 per cent].

*1-isoButylaminobenzthiazole hydrotribromide*.—A solution of *s*-phenylisobutylthiocarbamide (Hecht, *Ber.*, 1892, 28, 813), in chloroform (1 g. in 12 c.c.) was treated with bromine (0.8 c.c. in 0.8 c.c. of chloroform) and the mixture was heated and thereafter concentrated under reduced pressure at laboratory temperature, when a viscous liquid was obtained which crystallised on keeping. The *hydrotribromide* formed orange crystals, m.p. 98°. [Found: Br (total), 53.1; Br (labile), 33.1. Calc.: Br (total), 53.7; Br (labile), 35.8 per cent]. On reduction with sulphurous acid it gave 1-*iso*-butylaminobenzthiazole which separated from alcohol in glistening needles, m.p. 104°.

*5-Bromo-1-isobutylaminobenzthiazole hydropentabromide* (VI).—A solution of 1-*isobutylaminobenzthiazole* in chloroform (0.6 g. in 6 c.c.) was treated with bromine (0.4 c.c. in 0.4 c.c. of chloroform) and the solution was heated under reflux on a water-bath for 5 minutes and thereafter concentrated in a vacuum. The *hydropentabromide* then crystallised in the form of deep orange-red crystals, m.p. 76-77°. [Found: Br (total), 70.0; Br (labile), 45.0.  $C_{11}H_{13}N_2BrS \cdot HBr$  ( $Br_4$ ) requires Br (total), 70.0; Br (labile), 46.0 per cent]. On

reduction with sulphurous acid and basification with ammonia, it yielded 5-bromo-1-isobutylaminobenzthiazole which was identified by m.p. and mixed m.p. determinations with an authentic specimen prepared from *s-p*-bromophenylisobutylthiocarbamide (Hunter and Soyka, *loc. cit.*).

*1-isoAmylaminobenzthiazole hydrotribromide*.—Considerable difficulty was experienced in connexion with the bromination of *s*-phenyl-isoamylthiocarbamide in the earlier investigation, and the hydrotribromide of 1-isoamylaminobenzthiazole was analysed in the form of a resin (Hunter, *J. Chem. Soc.*, 1926, 2956). On this occasion, however, the red gum obtained from the bromination of *s*-phenylisoamylthiocarbamide under similar conditions to those used in the case of the isobutyl derivative, crystallised after keeping in a vacuum over potassium hydroxide for 2 days. The hydrotribromide obtained in this way had m.p. 61-62°. [Found: Br (total), 53.2; Br (labile), 33.0. Calc.: Br (total), 52.3; Br (labile), 34.4 per cent]. On reduction with sulphurous acid it yielded 1-isoamylaminobenzthiazole.

*s-Phenyl n-hexylthiocarbamide*, prepared from the condensation of phenylthiocarbimide with excess of *n*-hexylamine in alcohol, crystallised from alcohol in needles, m.p. 110° (previously recorded as 103-104°).

*1-n-Hexylaminobenzthiazole hydropentabromide*.—A solution of the phenylhexylthiocarbamide in chloroform (1.5 g. in 18 c.c.) was treated with bromine (1.2 c.c.) and the solution was heated and thereafter concentrated in a vacuum, when a hydropentabromide separated in red crystals which had m.p. 66-67° after being dried in the usual way. [Found: Br (total), 61.2; Br (labile), 48.8.  $C_{13}H_{18}N_2S$ . HBr (Br<sub>4</sub>) requires Br (total), 62.9; Br (labile), 50.3 per cent]. This compound was highly unstable and rapidly lost bromine on exposure to moist air or on keeping in a desiccator over potassium hydroxide. On reduction with sulphurous acid, it yielded 1-*n*-hexylaminobenzthiazole which had m.p. 67-68° after recrystallisation (previously recorded as 57°).

*s-Phenyl-n-heptylthiocarbamide*, prepared from phenylthiocarbimide and *n*-heptylamine, had m.p. 78° after recrystallisation (previously recorded as 70-71°). Unfortunately, the quantity of this compound available after purification was small (0.3 g.) and we were unable to make more than a preliminary examination of its bromination in the presence of excess of halogen. Under conditions similar to those employed in the case of the hexylthiocarbamide, it

gave rise to an indefinite orange bromo-addition compound, m.p. 73-74°. [Found: Br, 59·7.  $C_{14}H_{20}N_2S$ ,  $HBr (Br_3)$  requires Br, 56·2 and  $C_{14}H_{20}N_2S$ ,  $HBr (Br_4)$  requires Br, 61·6 per cent] On reduction with sulphurous acid, it yielded 1-*n*-heptylaminobenzthiazole which had m.p. 61-62° after recrystallisation (previously recorded as 55°).

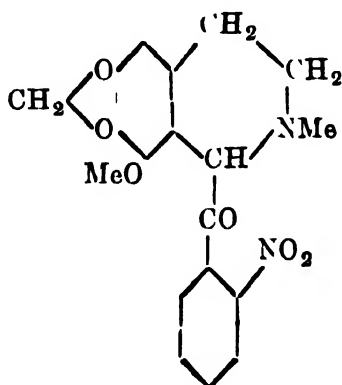
THE MUSLIM UNIVERSITY,  
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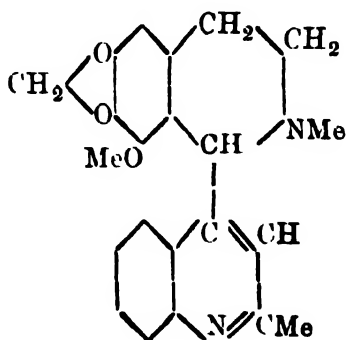
## Attempts to Prepare Antimalarials. Part IV. Derivatives of Cotarnine.

BY GURCHARAN SINGH AHLUWALIA, KANSHI NATH KAUL AND  
JÑANENDRA NATH RÂY.

It has been shown in Part III of this series of investigation (Ahluwalia, Kochhar and Rây, *J. Indian Chem. Soc.*, 1932, **9**, 215) that some derivatives of cotarnine show antipyretic properties *in vivo* and antiseptic properties *in vitro*. The present work is an extension of the investigation recorded in Part III. It was thought that if a quinoline ring could be fused to cotarnine then the antimalarial properties would be enhanced owing to partial similarity of structure to quinine. With this object, *o*-nitro aromatic aldehydes have been condensed with cotarnine to give the substance of the type (I). Following Robinson and Robinson (*J. Chem. Soc.*, 1914, **105**, 1458) the compound is formulated as (I).



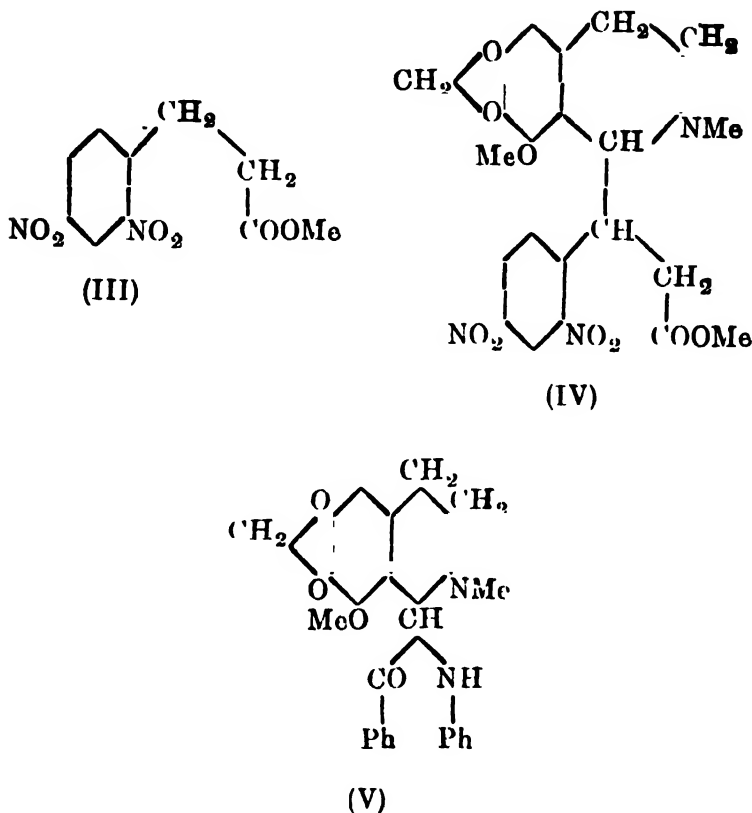
(I)



(II)

These substances can be easily reduced to the corresponding amino compounds under careful experimental conditions. The amine derived from (I) gives with acetone the cotarninoquinoline (II) in small yield.

It was thought that an *o*-nitro ester like (III) would easily condense with cotarnine to give a product (IV), which on reduction would furnish a cotarninoaminocarbostyryl



But the reduction of the substances of the type (IV) has not yet been satisfactorily accomplished.

The nitro esters (III, and analogous substances) on reduction are converted into aminotetrahydroquinolones (*cf.* Gabriel and Zimmermann, *Ber.*, 1879, **12**, 602). Clemons and Johnson (*J. Chem. Soc.*, 1930, 2138) have indicated that tetrahydroquinolone has local anæsthetic property. Watanabe (*J. Biochem., Japan*, 1930, **12**, 71) has studied the pharmacological properties of 7-amino-1:2:3:4-tetrahydroquinolone. We are now engaged in studying the local anæsthetic property of the dimethylaminobenzoyl derivative of this substance.

From the consideration that harmine is an antimalarial, it was intended to synthesise an anhydrocotarninoindole. For this purpose  $\omega$ -anilidoacetophenone and related substances were prepared and the



condensation with cotarnine to (V) was easily effected, but the subsequent ring closure to an indole could not be accomplished.

A number of condensation products of cotarnine with  $\omega$ -bromoacetophenone, resacetophenone (*cf.* Hope and Robinson, *J. Chem. Soc.*, 1918, 103, 873, who have condensed resacetophenone dimethyl-ether), aceto- $\alpha$ -naphthol, phenylurea, etc. were effected and are described in the experimental part.

#### EXPERIMENTAL.

A mixture of cotarnine (4.8 g.) and *o*-nitrobenzaldehyde dissolved in absolute alcohol (50 c. c.) was gently heated on the steam-bath for 20 minutes, when a yellow crystalline deposit began to separate. The product collected after some time was washed with cold alcohol and recrystallised from a mixture of benzene and alcohol, m. p. 164°. (Found: N, 7.7.  $C_{19}H_{18}O_6N_2$  requires N, 7.56 per cent).

The foregoing substance (3 g.) was well powdered and gradually added to a mixture of stannous chloride (5 g.), hydrochloric acid (d 1.16, 8 c. c.) and the mixture mechanically shaken for 10 hours and then diluted with water and filtered. The filtrate strongly basified (sodium hydroxide solution) furnished the amine which was collected and crystallised from benzene, m. p. 121°. (Found: N, 8.26.  $C_{19}H_{20}O_4N_2$  requires N, 8.23 per cent).

The amino compound (1 g.) dissolved in alcohol (10 c. c.) was boiled for 2 minutes with acetone (3 c. c.) and a drop of sodium hydroxide solution (50%) when a clear solution resulted. On keeping for a short time, a crystalline substance separated. It was collected and crystallised from alcohol, m. p. 133°. (Found: N, 8.2.  $C_{22}H_{22}O_3N_2$  requires N, 7.73 per cent).

Similarly cotarnine (4.8 g.), 3:4-dimethoxy-6-nitrobenzaldehyde (4.4 g.) in alcohol (20 c. c.) after heating for 15 minutes on the steam-bath, deposited the condensation product after 2 hours. Recrystallised from benzene and alcohol it melts at 165° (decomp.). (Found: N, 6.80.  $C_{21}H_{22}O_8N_2$  requires N, 6.5 per cent). The reduction to the corresponding amine could not be satisfactorily accomplished.

*Methyl-2:4-dinitrodihydrocinnamate* was prepared from the corresponding acid via the acid chloride. After crystallisation from methyl alcohol it melts at 40°. (Found: N, 11.3.  $C_{10}H_{10}O_6N_2$  requires N, 11.02 per cent).

A mixture of methyl-2:4-dinitrodihydrocinnamate (2.6 g.), and cotarnine (2.4 g.) in methyl alcohol (5 c. c.) was gently warmed on the steam-bath with piperidine (2 drops) till a complete solution resulted and then left for 4-5 hours at the room temperature (30°). The crystalline deposit after recrystallisation from hot methyl alcohol melted at 112-13°. (Found: N, 9.05.  $C_{22}H_{23}O_9N_3$  requires N, 8.8 per cent). This substance could not be reduced to a cotarninoquinoline.

6-Nitro-3:4-methylenedioxydihydrocinnamic acid (cf. Baker and Robinson, *J. Chem. Soc.*, 1925, 127, 1428) was formed when 3:4-methylenedioxydihydrocinnamic acid (5 g.) in acetic acid solution was nitrated at 0° with nitric acid (d 1.4, 8 c. c.). The nitration mixture after standing for 1 hour in a freezing mixture was poured on to crushed ice and the solids separated were crystallised from hot dilute methyl alcohol, m. p. 152°. (Found: N, 5.97.  $C_{10}H_9O_6N$  requires N, 5.85 per cent). The methyl ester of the nitro-acid, prepared in the usual way, had m. p. 72°. (Found: N, 5.75.  $C_{11}H_{11}O_6N$  requires N, 5.5 per cent).

Similarly  $\beta$ -piperonylpropionamide on nitration gave  $\beta$ -6-nitro-piperonylpropionamide, m. p. 186°. (Found: N, 12.0.  $C_{10}H_{10}O_5N_2$  requires N, 11.8 per cent).

*Condensation of cotarnine with  $\omega$ -bromoacetophenone in alcohol : Formation of  $\omega$ -ethoxy- $\omega$ -cotarninoacetophenone.*—Cotarnine dissolved in hot ethyl alcohol was treated with bromoacetophenone and the mixture heated for some time and then allowed to stand. After recrystallisation from hot ethyl alcohol bright yellow needles separated, m. p. 120°. The substance does not contain bromine and is obviously the substance figured in the title, as  $\omega$ -ethoxyacetophenone, condensed with cotarnine in a similar manner, furnished an identical product. (Found: N, 4.53.  $C_{34}H_{38}O_8N_2$  requires N, 4.6 per cent).

*Condensation of cotarnine with  $\omega$ -anilidoacetophenone.*—To a solution of  $\omega$ -anilidoacetophenone (2.2 g.) in hot ethyl alcohol, cotarnine (2.5 g.) was added and the product separated after standing for some time. Crystallised from benzene-ligroin it had m. p. 130° (decomp.). (Found: N, 6.6.  $C_{26}H_{26}O_4N_2$  requires N, 6.5 per cent).

Similarly,  $\omega$ -*p*-toluididoacetophenone furnished the corresponding anhydrocotarnino-*p*-toluididoacetophenone, m. p. 134°. (Found: N, 6.8.  $C_{27}H_{28}O_4N_2$  requires N, 6.8 per cent). The *m*-toluidido compound, m. p. 116°. (Found: N, 6.22. Calc.: N, 6.3 per cent).

All these compounds decomposed on attempted ring closure to an indole.

*Anhydrocotarnino-β-aceto-α-naphthol*.—Cotarnine (2·5 g.) and aceto-α-naphthol (2 g.) condensed in hot alcoholic solution without a condensing agent, m. p. 146°. (Found: N, 3·4.  $C_{24}H_{23}O_5N$  requires N, 3·45 per cent).

Similarly resacetophenone furnished the corresponding compound with cotarnine isolated as the hydrochloride, m. p. 191°. (Found: N, 3·4.  $C_{20}H_{22}O_5NCl$  requires N, 3·48 per cent).

*Anhydrocotarninophenylurea* was formed by the condensation of cotarnine (4·8 g.) and phenylurea (2·7 g.) in absolute alcohol (20 c. c.), m. p. 155°. (Found: N, 12·05.  $C_{19}H_{21}O_4N_3$  requires N, 11·83 per cent).

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## **The Fat from the Seeds of *Vateria Indica*, Linn.**

By S. V. PUNTAMBEKAR AND S. KRISHNA.

When our work on this fat was ready for publication, a paper on the same subject appeared in the Journal of the Society of Chemical Industry (1931, 50, 471r) wherein Miss Jones had shown the fatty acids to consist of palmitic, stearic, arachidic and oleic acids. Since these results were not in accordance with our findings, we considered it desirable to recheck our data. The results that we have obtained appear to indicate the presence of myristic, stearic, lignoceric, elaidic (*isooleic* ?) and oleic acids in the total acids from the fat and a careful search for palmitic and arachidic acids did not reveal their presence. We have, as well, observed some other differences between our results and those published by Miss Jones and consequently consider it desirable to submit our data for publication

*Vateria indica*, Linn (N. O. *Dipterocarpaceae*; Vern. *Safed damar*) "is a large handsome tree forming evergreen forests at the foot of the Western Ghats from Kanara to Travancore. The tree yields a resin of considerable value known as 'piney resin' which in its properties compares very favourably with amber, and like copal is considerably employed in making varnishes" (Watt, "Dictionary of Economic Products," Vol. 6, Part IV, p. 223). The seed is ovoid 2—2½" long with a hard white kernel which on pressing or boiling is reported to yield 50 % of a pale yellow fat known as 'piney tallow.' In consistency the fat is midway between tallow and wax and has hitherto been employed for candle manufacture and for adulterating 'ghee.' The authors have recently suggested that the fat can be used as vegetable tallow (*Indian Forester*, 1932, 53, 69) ; and since it contains nearly 59% of stearic acid it can also serve as a convenient source of stearic acid.

The fat has been studied for its chemical and physical constants (Höhnel and Wolfbauer, *Pharm. Centralh.*, 1886, 26, 857 ; Crossley and Le Sueur, *J. Soc. Chem. Ind.*, 1898, 17, 993 ; *Bull. Imp. Inst.*, 1930, 43, 280) but no systematic study appears to have been made of its chemical composition except that by Dal Sie (*Gazzetta*,

1896, 8, 107) and Miss Jones (*loc. cit.*), the results of both being at variance with ours. According to Dal Sie, who arrived at his conclusions mainly by the melting points of the acids obtained by fractional precipitation of the barium salts of the mixed acids, the fat consists of glycerides of palmitic acid (75 %) and oleic acid (25%), whereas Miss Jones records the components of the fatty acids as palmitic (10%), stearic (89%), arachidic (3%) and oleic acid (48%). Our results on the other hand indicate that the fat consists mainly of the glycerides of stearic (59 %), elaidic (*isooleic* ?) and oleic acids 89%) (Höhnel and Wolfbauer, *loc. cit.*).

The *Vateria indica* seeds, used in this investigation, were obtained from Mangalore. The kernels, on separation from the shells, were dried, powdered and expressed at 50—60° in a hydraulic press, which gave 14% of the fat ; and a further 8% was obtained from the meal on extraction with light petroleum. The average yield was between 20—22% (Bolton, "Oils, Fats and Fatty Foods," 1928, p. 267 and *Bull. Imp. Inst., loc. cit.*) and never as high as 50% as reported in some of the earlier works (Watt, *loc. cit.*). For determination of the physical and chemical constants, the freshly expressed fat was employed. The pale yellow colour of the fat is bleached on standing and iodine value is lowered. In some of the samples that had been standing exposed to air for a few weeks, the iodine value fell from 40 to 20.

#### *General Characteristics of the Fat.*

Consistency	...	tallow like.
Colour	...	pale yellow when fresh, white on standing.
M. p.		40°
Sp. gr. at 20°	.	0.9120
Refractive index at 25°	..	1.4536
Saponification value		190.4
Iodine value (Hanus)		40.0
Acetyl value	.	2.45
Höbner value	. .	97.6
Acid value	..	1.4
Unsaponifiable matter	...	0.8 per cent.

*Composition of the Fatty Acids.*

Preliminary examination of the mixed fatty acids indicated the presence of a large percentage of stearic acid, the major portion of which was consequently removed by repeated crystallisation with 95% alcohol instead of the 70% (Armstrong, Allen and Moore, *J. Soc. Chem. Ind.*, 1925, **44**, 641). The remaining acids were then separated into the solid and the liquid acids by the usual lead salt-alcohol method (Twitchell, *Ind. Eng. Chem.*, 1921, **13**, 806). The presence of a large percentage of solid acids both saturated and unsaturated (Cocks, Christian and Harding, *Analyst*, 1931, **56**, 368) in the total acids made it difficult to effect complete separation by a single Twitchell's procedure and therefore it had to be repeated thrice before a reasonably complete separation was possible. The solid and the liquid acids were then converted into their methyl esters and further separated into fractions by distillation under reduced pressure and the fractions singly examined. The results obtained in this manner are tabulated and discussed below.

*Chemical Constants of the Mixed Fatty Acids.*

Mean molecular weight	...	286
Iodine value	...	38.6
Saturated acids	...	61%
Unsaturated acids	...	39%

280 G. of the crude fatty acids were treated with a slight excess of sodium hydroxide and the resulting soap was incorporated with filter paper pulp. The mass was dried, powdered and extracted with ether in a Soxhlet and the extract examined for the unsaponifiable matter, as described later.

*Saturated Acids.*

287 G. of the mixed acids from which the unsaponifiable matter had been removed were crystallised several times from 95% alcohol and 70 g. of an acid (m. p. 68°-9°; M. W. 283.3; Iodine value 0.5) was isolated. This was identified as stearic acid by its mixed melting point with an authentic sample.

The remaining 167 g. of the acids in the mother liquor were separated twice into solid and liquid acids by the Twitchell's

method. The following Table shows the state of separation of the different acids after the above two separations.

Method.	Acids.	Iodine value.	M. W.	Net weight.
Crystallisation	Stearic	0.5	283.3	70 g.
Twitchell's	(A) Solid (1st Twitchell)	3.6	280.0	63.5
	(B) Solid (2nd Twitchell)	18.6	280.0	5.5
	(C) Liquid	58.0	280.0	98.0

*Solid Acids (A).*—These were converted into their methyl esters and the unesterified acids removed by 5% sodium carbonate. 53.1 G. of the neutral esters were fractionated at 5-7 mm. pressure with the following results. The acids liberated from each of the fractions were fractionally crystallised for identification purposes.

Fractions.	B.p.	Weight.	M.W. of the acids.	Component of the esters.		
				Methyl myristate.	Methyl stearate.	Methyl lignocerate
S <sub>1</sub>	125-180	4.15 g.	266.0	1.33 g.	2.82 g.	...
S <sub>2</sub>	180-85	6.50	275.0	1.06	5.44	...
S <sub>3</sub>	185-87	17.87	280.0	...	17.87	...
S <sub>4</sub>	187-90	12.40	282.0		12.40	..
S <sub>5</sub>	190-95	9.59	284.6	...	9.59	.
Residue	...	1.98	335.5	..	0.74	1.24 g.
Loss	...	0.61	...	...	...	...
Total	...	53.1	...	2.39	48.86	1.24

*Fraction S<sub>1</sub>.*—Three crystallisations from acetone gave an acid (m.p. 68-69°; M. W. 283.2) which was identified as stearic acid by its mixed melting point with an authentic sample. The mother liquors on successive concentration and removal of the crystalline product gave a residue, m.p. 49-51° and M. W. 262.

*Fraction S<sub>2</sub>.*—Two crystallisations from acetone yielded an acid which was identified as stearic acid. The mother liquor on succe-



sive concentration and removal of the crystalline product gave a residue, M. W. 262.5.

*Fractions S<sub>3</sub>, S<sub>4</sub> and S<sub>5</sub>.*—These fractions were identified as pure stearic acid, m.p. 68-69°; M. W. 284.5 and methyl ester, m.p. 38-39°.

The residue was a dark brown viscous mass, apparently consisting of a mixture of stearic and some higher solid acids along with their decomposition products. On crystallising thrice from 95% alcohol it yielded crystals, m.p. 77-78°, M.W. 368.6 with no change in the melting point on further crystallisation. Its mixed melting point with a sample of lignoceric acid from another source (Katti and Manjunath, *J. Indian Chem Soc.*, 1929, 6, 844) remained unchanged. Stearic acid was also isolated from the mother liquor and the residue being a complex, viscous and highly coloured mass was not identified further.

Palmitic acid, if at all it is present in the fatty acids, should have been found in the fractions S<sub>1</sub> and S<sub>2</sub> and in the solid acids (B) and (B<sub>1</sub>) but no indication of its presence was found. The lower acid (m.p. 49-51°; M.W. 262), present in these fractions, on the other hand, appears to be myristic acid since its melting point is much lower than the melting point (55°) of the eutectic mixture of palmitic and stearic acids (Lewkowitsch "Chemical Technology and Analysis of Oils, Fats and Waxes" 1921, Vol. I, p. 120).

*Solid acids (B).*—The mother liquor, from which the lead salts of the solid acids (A) had been separated, was concentrated to half its volume and then treated with the same volume of a hot alcoholic solution of lead acetate (20 g.) and the mixture allowed to stand overnight at 15-16°. The amount of precipitate thus obtained yielded 5.5 g. of solid acids (B) which on crystallisation from 95 % alcohol gave an acid m p 68-69° and M.W. 284.2. This was identified as stearic acid. Further quantity of stearic acid was obtained from the mother liquor by concentration. The residue, a brown viscous mass, had an iodine value 26 and M.W. 300. This appeared to contain oleic acid, which explains the high iodine value. The high molecular weight might possibly be due to the portion of the acids having got esterified during repeated crystallisations.

The above analyses lead us to conclude that the solid acids consist mainly of stearic acid with small amounts of myristic (not isolated) and lignoceric acid (isolated). Palmitic and arachidic acids as

reported by Miss Jones (*loc. cit.*) were not found. It is not clear from the brief data of her analysis whether she actually isolated and identified these acids or merely calculated their presence from the mean molecular weight of the fractions in which their presence was assumed. The latter procedure, it might be pointed out, is not perfect and in many cases leads to erroneous conclusions.

### *Unsaturated Acids*

The liquid acids (C) were saponified to break up the esters which might have been formed in the alcohol treatment and the liberated acids when dissolved in ether, deposited a white solid (1.5 g) which on crystallisation from 95% alcohol melted at 130° and had M. W. 316. This appears to be dihydroxystearic acid resulting from the atmospheric oxidation of the oleic acid or its isomers present in the liquid acids. The liquid acids, isolated from the ether solutions, had at this stage an iodine value of 57.6 and M. W. 280.

A portion of the acids on bromination (Lewkowitsch "Chemical Technology and Analysis of Oils, Fats and Waxes" Vol. I, 6th edition, p. 595) gave no hexabromides, nor could any tetrabromide be isolated. Another portion was converted into its potassium soap and oxidised by a dilute potassium permanganate solution according to the method of Lapworth and Mottram (*J. Chem. Soc.*, 1925, 127, 1628). The oxidised product was identified as dihydroxystearic acid (m.p. 130-32°; M. W. 316) and the unoxidised portion (23%) was left as a viscous mass of mean M. W. 306.8 and the iodine value 7.8. A third portion of the acids was converted into potassium soap and oxidised by a concentrated solution of potassium permanganate according to the method of Bertram as modified by Hilditch and Priestman (*Analyst*, 1931, 56, 354; Smith and Chibnall, *Biolo. J.*, 1932, 26, 222). The unoxidised acids obtained after magnesium salt separation (10%) melted at 57-58° and had a M. W. of 288.

The above three experiments indicate that the unsaturated acids in the liquid portion (C) consist entirely of oleic acid or its isomers and that the acids of more than one double bond namely, linoleic, linolenic, etc., are absent. They also indicate that the liquid acids still contain some solid acids, portion of which is stearic acid as shown by Bertram's oxidation. The slightly higher molecular weight namely 288 is in all probability due to the incomplete destruction of the dihydroxystearic acid (Gay, *J. Soc. Chem. Ind.*, 1932,

51, 126r). The balance of the substance, removed in Bertram's oxidation, appears to be of high molecular weight (M. W. 306·8, apparently dihydroxystearic acid) as shown by the oxidation method of Lapworth and Mottram (*loc cit.*).

*Third Twitchell's separation.*—64·25 G. of the de-esterified liquid acids were separated into solid and liquid acids and these were obtained in the following proportion.

Acids.	Wt.	Iodine value.	M. V
Solid acids (B <sub>1</sub> )	11·9 g.	96·05	281
Liquid acids	52·35	63·90	288

The solid acids on crystallisation from 75% alcohol gave a product, m.p. 63-64° and M. W. 281·7. This was identified as stearic acid by its mixed melting point with a pure sample.

The liquid acids (52·35 g.), on standing, deposited a quantity of dihydroxystearic acid and even after removal of this the iodine value remained low (64). This indicated the presence of some saturated acids and consequently the liquid acids were submitted to Twitchell's method, once again.

*Fourth Twitchell's separation.*—The state of separation after this stage was as follows.

Acids.	Wt	Iodine value.	M. W.
Solid acids	13·25 g.	80·4	282·7
Liquid acids	32·10	56·6	326·5
Dihydroxystearic acid	2·00		316·8

On twice crystallising from acetone, the solid acids yielded transparent plates, m.p. 43-44°, M.W. 284 and iodine value 85. This appeared to be elaidic acid (*isoleic acid* ?). The iodine value and the mean molecular weight of the liquid part indicated that it was still associated with some saturated substance.

The liquid acids were saponified by alcoholic potash to remove any ethyl esters and the resulting acids converted into methyl esters in the usual way. The esters on being dissolved in ether deposited a white solid, m. p. 63-64° (methyl ester of an isomeric dihydroxystearic acid). After removing this and the solvent ether, the 21·28 g. of the esters were fractionated at 3-5 mm. pressure with the following results:

Fractions.	B. p.	Weight.	Iodine value.	Component of the esters.	
				Methyl elaidate or oleate	Methyl ester of dihydroxy stearic acid.
L <sub>1</sub>	75-120	0.93 g.	10.2	—	—
L <sub>2</sub>	172-75	6.19	82.1	6.19 g.	—
L <sub>3</sub>	175-79	6.38	89.2	6.38	—
L <sub>4</sub>	179-85	2.12	74.4	1.84	0.28 g.
L <sub>5</sub>	185-240	2.26	35.7	0.94	1.32
Residue	—	2.90	38.0	1.28	1.62
Loss	—	0.50	—	—	—
Total	—	21.28	—	16.63	3.22

*Fraction L<sub>1</sub>* was too small for further investigation. It appeared to consist of some low boiling substance probably an ester of a saturated acid of low molecular weight and a little methyl oleate.

*Fractions L<sub>2</sub> and L<sub>3</sub>* appeared to be oleic acid. It cannot be said that the previous treatment was sufficient to completely remove the elaidic (isoleic?) from oleic acid hence it is not possible to say what fractions are exactly those of pure oleic acid.

*Fraction L<sub>4</sub>* was mostly methyl oleate. On standing it deposited a white crystalline substance, m. p. 67-68°, soluble in cold concentrated sulphuric acid and insoluble in alkali and only slightly soluble in petroleum ether. This appears to be the methyl ester of an isomeric dihydroxystearic acid. After removal of this, the iodine value of the fraction rose to 77. The fraction deposited again the same solid matter after standing for a couple of days. The above substance on saponification and liberation of the corresponding acid gave from acetone a crystalline product, m. p. 90-91°, M. W. 810. This appears to be dihydroxystearic acid, an oxidation product of elaidic acid. It might be pointed out here that the literature records the melting point of dihydroxystearic acid as 99-100° (Saytzeff, *J. pr. Chem.*, 1888, 33, 315) and also as 95.6° (Arnaud and Posternak, *Compt. rend.*, 1910, 150, 1180.)

*Fraction L<sub>5</sub>* was almost solid. It appeared to contain some methyl oleate,

The residue was a viscous dark mass which appeared to be a mixture of methyl oleate and the substance isolated in fractions  $L_4$  and  $L_5$  and some decomposed matter.

The above data on calculation gives the following percentage composition for the fatty acids :

Acids.	Wt.	%.
Myristic	2.76 g.	1.16
Stearic	139.25	58.76
Lignoceric	1.46	0.62
Elaidic ( <i>isooleic</i> ?)	32.10	13.55
Oleic and elaidic ( <i>isooleic</i> ?)	44.23	18.66
Dihydroxystearic		
(calculated as oleic acid)	8.43	3.55
Isomeric dihydroxystearic acid (calculated as oleic acid)	8.77	3.70
Total	237.00	100.00

#### *Unsaponifiable Matter.*

From alcohol the unsaponifiable matter deposited a curdy material, which after two crystallisations yielded a product melting at 75–77°. Under the microscope it appeared to consist partly of needle-like crystals and partly of a substance retained in the mother liquor. It gave no test for a sterol. In cold concentrated sulphuric acid it slowly developed a yellow colouration but the bulk remained insoluble. The amount of the substance being very small further identification was not possible.

The filtrate of this substance after standing overnight was found to deposit a granular substance which after three crystallisations yielded colourless plates, m. p., 133–34°. It gave all the characteristic colour tests of phytosterol and an acetate melting at 118–19°. The melting point of the substance and that of its acetate indicated its identity with sitosterol.

#### SUMMARY.

The fat from the seeds of *Vateria indica* has been found to contain the glycerides of myristic, stearic, lignoceric, elaidic (*isooleic*?) and oleic acids together with sitosterol melting at 133–34°. The presence of palmitic and arachidic acids has not been detected.



# On the Study of Polyhalides. Part II. Formation and Dissociation of Chloro-dibromides and Tri-bromides of Sodium, Potassium, Strontium and Barium.

BY SUSIL KUMAR RAY.

Polyhalides of the alkali metals have been the subject of numerous investigations and polyhalides of rubidium, caesium and ammonium, stable at ordinary temperatures have long been known. Some references to the literature of the polyhalides of the alkali metals were given in the first part of this work (Ray, *J. Indian Chem. Soc.*, 1952, 9, 259). So far the formation of alkali polyhalides have been studied with the aid of the solubility, partition, conductivity and spectroscopic experiments. In the present paper, the formation and dissociation of the polyhalogen compounds of the metals of the alkali and alkaline earths have been studied with the aid of the freezing point method (*cf.* Ray, *loc. cit.*). It has been shown that the formation of the polyhalogen compounds like  $\text{NaClBr}_2$ ,  $\text{KClBr}_2$ ,  $\text{Sr}_2\text{ClBr}_2$ ,  $\text{Ba}_2\text{ClBr}_2$ ,  $\text{NaBr}_3$ ,  $\text{KBr}_3$ ,  $\text{Sr}_2\text{Br}_3$  and  $\text{Ba}_2\text{Br}_3$  can be definitely established by this method. The reactions were always studied in dilute solutions ( $N/2$  to  $N/16$ ) and with moderate concentrations of halogens. The action of iodine on the chlorides could not be studied owing to the sparing solubility of iodine in the dilute solutions of the chlorides.

The equilibrium constants of the reactions



and

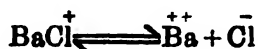


(where X stands for Na, K,  $\frac{1}{2}\text{Sr}$  or  $\frac{1}{2}\text{Ba}$ ) or expressed ionically



and the heats of formation of the complexes  $\text{ClBr}_2$  and  $\text{Br}_2$  have been calculated on the basis of the above equations.

The interaction between the halogens and the halides of strontium and barium cannot be represented, owing to the ionisation of these halides by stages, in the above simple way. The reaction for instance, between bromine and barium chloride can be expressed in the following way:



In very dilute solutions the normal reaction (i) takes place. In concentrated solutions of  $\text{BaCl}_2$ , the conversion of  $\text{BaCl}_2$  into

$\text{Ba}^{++}$  and  $\text{Cl}^-$  ions may not be complete and the reaction may take place to a certain extent according to the scheme (ii). Besides, the reaction may also be molecular (iii). It will be noticed that in the case of strontium and barium, the equilibrium constants are found to vary to a certain extent. The reason being that the degree of dissociation of the halides of the metals of the alkaline earths being small in comparison with that of the alkali metals, the change in their degree of dissociation by the formation of the complexes cannot be neglected. Besides the likely formation of  $\text{BaCl}_2\text{Br}_2$  and the higher complexes (the solution becoming sufficiently concentrated at the low temperature) would lead to some complications. Moreover, there is also some likelihood of hydrolysis taking place.

In the following experiments the calculation of the equilibrium constants, the degree of dissociation of the halides, the heats of formation of the complexes, etc., were calculated as in the first part of this work (*loc. cit.*).

The method of procedure is practically identical with that described in the first part of this paper for polyhalides of hydrogen (*loc. cit.*).



TABLE I.

*Formation of NaClBr<sub>2</sub>.*

	Depression actual.	Depression calc.	Conc. of Br in g. per 25 c.c.	Equilibrium constant <i>K</i> .	Dissocia- tion con- stant 1/ <i>K</i> .	Degree of dissociation <i>a</i> <sub>2</sub> .
<i>N</i> /2-NaCl	1·795	0·929	0·0	.	...	...
<i>N</i> /2-NaCl + Br <sub>2</sub>	0·070	0·2179	0·4691	5·478	0·1825	0·3212
„	0·030	0·1564	0·3367	5·217	0·1918	0·3196
„	0·042	0·1376	0·2962	5·505	0·1817	0·3062
<i>N</i> /4-NaCl	0·910	0·4645	0·0	...	...	...
<i>N</i> /4-NaCl + Br <sub>2</sub>	0·120	0·2401	0·5169	5·738	0·1743	0·4996
„	0·107	0·2179	0·4690	5·773	0·1782	0·4910
„	0·080	0·1623	0·3494	5·293	0·1889	0·4927
<i>N</i> /8-NaCl	0·460	0·2322	0·0	..	...	...
<i>N</i> /8-NaCl + Br <sub>2</sub>	0·157	0·2351	0·5059	5·913	0·1691	0·6677
„	0·125	0·1905	0·4102	5·853	0·1709	0·6561
„	0·065	0·1042	0·2245	5·843	0·1712	0·6237
<i>N</i> /16-NaCl	0·230	0·1160	0·0	...	...	...
<i>N</i> /16-NaCl + Br <sub>2</sub>	0·150	0·1880	0·4048	6·095	0·1641	0·7979
„	0·105	0·1324	0·2852	5·542	0·1804	0·7930
„	0·067	0·0871	0·1877	5·802	0·1724	0·7686

Mean value of *K* = 5·654. Mean value of 1/*K* = 0·1769. Mean temp. = -0·94°.

TABLE II.

*Formation of KClBr<sub>2</sub>.*

	Depression actual.	Depression calc.	Conc. of Br in g. per 25 c.c.	Equilibrium constant K.	Dissocia- tion con- stant 1/K.	Degree of dissocia- tion $\alpha_2$ .
N/2-KCl	1·805	0·929	0·0	...	...	...
N/2-KCl + Br <sub>2</sub>	0·075	0·2444	0·5261	5·691	0·1697	0·3069
„	0·062	0·2033	0·4378	5·781	0·1730	0·3049
„	0·040	0·1924	0·2852	5·895	0·1651	0·3020
N/4-KCl	0·915	0·4645	0·0	...	...	...
N/4-KCl + Br <sub>2</sub>	0·107	0·2222	0·4785	5·973	0·167	0·1816
„	0·080	0·1795	0·3864	5·915	0·168	0·1158
„	0·070	0·1479	0·3183	5·549	0·180	0·4735
N/8-KCl	0·465	0·2322	0·0	...	...	...
N/8-KCl + Br <sub>2</sub>	0·137	0·2068	0·4452	5·711	0·174	0·6624
„	0·105	0·1590	0·3422	5·657	0·177	0·6606
„	0·080	0·1247	0·2686	5·577	0·179	0·6412
N/16-KCl	0·230	0·116	0·0	...	...	...
N/16-KCl + Br <sub>2</sub>	0·115	0·1636	0·3522	5·926	0·1691	0·7030
„	0·105	0·1316	0·2833	5·619	0·1781	0·7979
„	0·080	0·1017	0·2190	5·315	0·1882	0·7866

Mean value of  $K = 5·739$ . Mean value of  $1/K = 0·174$ . Mean temp =  $-0·98^\circ$ .

The value of the dissociation constant as obtained by Job (*Ann. Chim.*, 1928, *x*, 9, 148), at  $16^\circ$  is 0·190. The heat of formation of ClBr<sub>2</sub> ion was calculated between the temperatures,  $-0·98^\circ$  and  $16^\circ$  (Job) and was found to be 798 calories; the value obtained by other investigators are as follows: Job (*loc. cit.*) from KClBr<sub>2</sub>, 1000 calories and Ray (*loc. cit.*) from HClBr<sub>2</sub>, 1044 calories.

TABLE III.  
*Formation of  $\text{Sr}_3\text{ClBr}_2$ .*

	Depression actual.	Depression calc.	Conc. of Br in g. per 25 c.c.	Equilibrium constant K.	Dissocia- tion con- stant $1/K$ .	Degree of dissocia- tion $\alpha_2$ .
$N/4\text{-SrCl}_2$	0.675	0.4645	0.0	...	...	...
$N/4\text{-SrCl}_2 + \text{Br}_2$	0.125	0.2188	0.4710	12.02	0.0832	0.5714
„	0.065	0.1274	0.2742	12.11	0.0826	0.5104
„	0.055	0.1026	0.2208	10.00	0.100	0.5363
$N/8\text{-SrCl}_2$	0.375	0.2322	0.0	...	...	...
$N/8\text{-SrCl}_2 + \text{Br}_2$	0.125	0.1846	0.3974	10.68	0.0917	0.6772
„	0.095	0.1453	0.3127	10.70	0.0934	0.6539
$N/16\text{-SrCl}_2$	0.230	0.116	0.0	...	...	...
$N/16\text{-SrCl}_2 + \text{Br}_2$	0.090	0.1265	0.2723	10.10	0.0992	0.7115
„	0.057	0.0863	0.1858	10.48	0.0955	0.6604

Mean value of  $K = 10.90$ . Mean value of  $1/K = 0.0918$ . Mean temp. =  $-0.51^\circ$ .

TABLE IV.  
*Formation of  $\text{Ba}_3\text{ClBr}_2$ .*

	Depression actual.	Depression calc.	Conc. of Br in g. per 25 c.c.	Equilibrium constant K.	Dissocia- tion con- stant $1/K$ .	Degree of dissocia- tion $\alpha_2$ .
$N/4\text{-BaCl}_2$	0.615	0.4615	0.0	...	...	...
$N/4\text{-BaCl}_2 + \text{Br}_2$	0.135	0.2240	0.4820	13.53	0.0739	0.6029
„	0.100	0.1675	0.3606	11.35	0.0881	0.5970
„	0.040	0.0786	0.1692	12.70	0.0787	0.5068
$N/8\text{-BaCl}_2$	0.330	0.2322	0.0	...	...	...
$N/8\text{-BaCl}_2 + \text{Br}_2$	0.115	0.1590	0.3422	13.34	0.0750	0.7235
„	0.060	0.0888	0.1914	13.06	0.0767	0.6751
$N/16\text{-BaCl}_2$	0.215	0.1160	0.0	...	...	...
$N/16\text{-BaCl}_2 + \text{Br}_2$	0.100	0.1402	0.3017	12.74	0.0785	0.7186
„	0.060	0.0914	0.1969	14.49	0.0690	0.6561

Mean value of  $K = 13.08$ . Mean value of  $1/K = 0.0767$ . Mean temp. =  $-0.48^\circ$ .

TABLE V.

*Formation of NaBr<sub>3</sub>.*

	Depression actual.	Depression calc.	Conc. of Br in g. per 25 c.c.	Equilibrium constant K.	Dissocia- tion con- stant 1/K.	Degree of dissocia- tion $\alpha_3$ .
N/4-NaBr	0.925	0.4645	0.0	...	..	...
N/4-NaBr + Br <sub>2</sub>	0.067	0.2679	0.5766	22.63	0.0442	0.2450
..	0.057	0.2478	0.5835	23.15	0.0432	0.2896
..	0.037	0.1768	0.3807	21.98	0.0455	0.2091
N/8-NaBr	0.465	0.2322	0.0	...	.	..
N/8-NaBr + Br <sub>2</sub>	0.110	0.2418	0.5206	22.28	0.0449	0.4548
..	0.077	0.1888	0.4065	22.55	0.0443	0.4078
..	0.032	0.0972	0.2098	22.86	0.0438	0.3284
N/16-NaBr	0.235	0.1160	0.0	..	...	...
N/16-NaBr + Br <sub>2</sub>	0.122	0.1897	0.4084	21.60	0.0464	0.6431
..	0.080	0.1368	0.2944	23.50	0.0425	0.5851
..	0.045	0.0881	0.1895	23.41	0.0421	0.5112

Mean value of  $K = 22.66$ . Mean value of  $1/K = 0.0441$ . Mean temp. =  $-0.65^\circ$ .

\* The values of the dissociation constants obtained by Griffith, McKeown and Winn (*loc. cit.*) are as follows:  $1/K$  at  $16.5^\circ$ , 0.0560 and  $1/K$  at  $21.5^\circ$ , 0.0598.

The heat of formation of Br<sub>3</sub> ion was calculated between the temperatures  $-0.65^\circ$  and  $21.5^\circ$  (Griffith, McKeown and Winn, *Trans. Faraday Soc.*, 1932, 28, 101) and was found to be 1917 calories. This is of the same order as those found by other investigators as given below :

Berthelot ( <i>Compt. rend.</i> , 1882, 94, 1618)	...	...	1990 calories.
Lewis and Randall ( <i>J. Amer. Chem. Soc.</i> , 1916, 38, 1616) from KBr <sub>3</sub>	1650	..	
Job ( <i>loc. cit.</i> )	...	from KBr <sub>3</sub>	2060 ..
Ray ( <i>loc. cit.</i> )	...	from HBr <sub>3</sub>	1467 ..

TABLE VI.  
Formation of  $\text{KBr}_3$ .

	Depression actual.	Depression calc.	Conc. of Br in g. per 25 c.c.	Equilibrium constant $K$ .	Dissociation constant $1/K$ .	Degree of dissociation $\alpha_2$ .
$N/4\text{-KBr}$	0.920	0.4645	0.0	...	...	...
$N/4\text{-KBr} + \text{Br}_2$	0.052	0.2308	0.4967	23.17	0.0432	0.2253
..	0.040	0.1897	0.4084	22.06	0.0453	0.2061
..	0.027	0.1401	0.3017	22.81	0.0438	0.1927
$N/8\text{-KBr}$	0.470	0.2322	0.0	..	...	...
$N/8\text{-KBr} + \text{Br}_2$	0.107	0.2401	0.5169	23.44	0.0427	0.4457
..	0.080	0.1940	0.4177	22.52	0.0444	0.4124
..	0.047	0.1294	0.2723	22.63	0.0440	0.4349
$N/16\text{-KBr}$	0.230	0.116	0.0	...	...	...
$N/16\text{-KBr} + \text{Br}_2$	0.185	0.2077	0.4471	23.27	0.0430	0.6500
..	0.097	0.1598	0.3441	22.77	0.0439	0.6019
..	0.057	0.1052	0.2263	23.16	0.0422	0.5422

Mean value of  $K = 22.87$ . Mean value of  $1/K = 0.0437$ . Mean temp. =  $-0.65^\circ$ .

The values of the dissociation constants, obtained by other investigators are given below:

Jones and Hartmann ( <i>J. Amer. Electrochem. Soc.</i> , 1916, 20, 295)	...	0.051 at $0^\circ$
Jakowkin, (calculated by Lewis and Randall, <i>loc. cit.</i> )	...	0.062 at $25^\circ$
Worley (calculated by Linhart, <i>J. Amer. Chem. Soc.</i> , 1918, 40, 158)	0.063	at $26.5^\circ$
Worley ( <i>J. Chem. Soc.</i> , 1905, 87, 1107)	...	0.065 at $32.5^\circ$
Griffith, McKeown and Winn ( <i>loc. cit.</i> )	{ 0.056 at $16.5^\circ$ 0.0576 at $21.5^\circ$	

The heat of formation was calculated between the temperatures  $-0.65^\circ$  and  $21.5^\circ$  (Griffith and others) and was found to be 1976 calories, which agrees very closely with the values obtained by other investigators (*loc. cit.*).



From a comparison of the equilibrium constants of the reactions involving the formation of  $\text{ClBr}_2$ ,  $\text{ClI}_2$ ,  $\text{Br}_3$ ,  $\text{BrI}_2$ , and  $\text{I}_3$  ions it will be seen that the equilibrium constant for the same complex ion varied with the nature of the cation of the halide employed. This is evident from the values tabulated below:

*Value of Equilibrium Constants.*

	Cations.		
	H.	Na.	K.
$\text{ClBr}_2$	1.726 <sup>1</sup>	5.654	5.739
	(-1.5°)	(-1°)	(-1°)
	1.412 <sup>2</sup>		5.263 <sup>3</sup>
	(30°)		(16°)
$\text{ClI}_2$	1.836 <sup>1</sup>		3.571 <sup>3</sup>
	(-3.8°)		(16°)
	1.60 <sup>2</sup>	1.961 <sup>4</sup>	2.325 <sup>4</sup>
	(25°)	(25°)	(25°)
$\text{Br}_3$	20.515 <sup>1</sup>	22.66	22.87
	(-1°)	(-0.6°)	(-0.6°)
		16.86 <sup>6</sup>	17.36 <sup>6</sup>
		(21.5°)	(21.5°)
	16.25		16.13 <sup>5</sup>
	(25°)		(25°)
$\text{BrI}_2$			18.52 <sup>3</sup>
			(16°)
	14.26 <sup>3</sup>		12.99 <sup>4</sup>
	(30°)		(25°)
	772.7 <sup>4</sup>	720.9 <sup>4</sup>	719.4 <sup>4</sup>
	(25°)	(25°)	(25°)

These divergences in the values of the equilibrium constants become strikingly evident from the following curves, obtained by

<sup>1</sup> Ray (*loc. cit.*).

<sup>2</sup> Ray and Sarkar (*J. Chem. Soc.*, 1922, 21, 1140).

<sup>3</sup> Job (*loc. cit.*).

<sup>4</sup> Jakowkin (*Z. physikal. Chem.*, 1896, 20, 19).

<sup>5</sup> Lewis and Randall (*loc. cit.*).

<sup>6</sup> Griffith, McKeown and Winn (*loc. cit.*).

plotting the values of the equilibrium constants against the respective ionic radii. The values of the ionic radii for  $\text{Na}^+$  ( $0.98\text{\AA}$ ) and

FIG. 1.

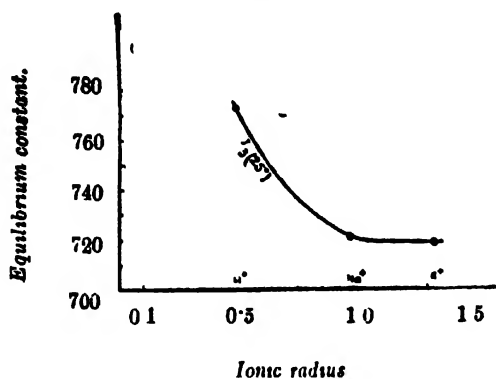
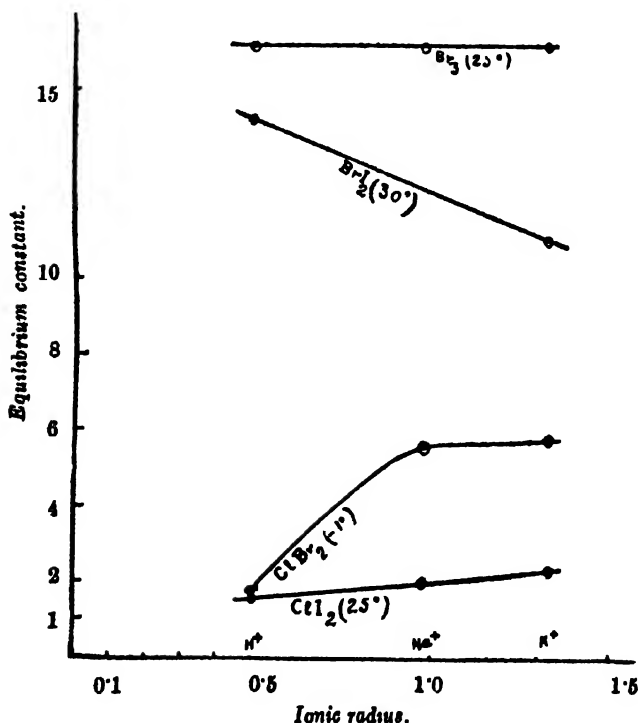


FIG. 2.



$\text{K}^+$  ( $1.38\text{\AA}$ ) were taken from Goldschmidt (*Trans. Faraday Soc.*, 1926, 26, 262). The ionic radius of  $\text{H}^+$  being assumed to be less than that for  $\text{Li}^+$  ( $0.76\text{\AA}$ ) and was taken to be  $0.5\text{\AA}$ . Slight temperature differences were neglected. The values of  $\text{Br}_2$  (at  $25^\circ$ ) and



$\text{BrI}_2$  (at  $80^\circ$ ), in presence of sodium ion and potassium ion respectively, were calculated from data quoted above.

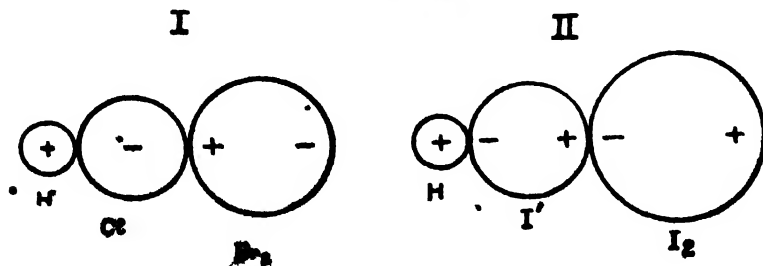
As it is intended only to indicate the influence of cationic volume upon the stability of any complex polyhalide ion formed, the nature of the curve or the relative values of the equilibrium constants are not in any way affected by tracing the curves for different temperatures for different complex ions.

It was assumed that the above reactions are all ionic, the constancy of the value of the equilibrium constants being obtained on that assumption. Thus for the formation of the complex ions, for instance  $\text{ClBr}_2$ , the value of the equilibrium constant on this assumption should remain unchanged, irrespective of the nature of the cation, but actually they are found to differ. It will further be noticed, that in the case of the chloro-dibromo ions, this difference is the greatest; it then decreases and practically vanishes in the case of  $\text{Br}_3$  ion, the differences again becoming pronounced in the case of  $\text{BrI}_2$  and  $\text{I}_3$  ions but in the opposite direction. This peculiar phenomenon cannot be explained by the assumption that the reaction is also to a certain extent molecular, the halide being completely dissociated in the dilute solutions employed.

The influence of this cationic volume upon the stability of the complex polyhalogen ion can be explained when not only the volume of the cation, but also the polarisability of the halogen molecule as well as that of the halogen ion is taken into consideration. As is well known, the polarisability of the halogen molecules and the halogen ions increases with their atomic volume, *i.e.*, in the order chlorine  $\rightarrow$  bromine  $\rightarrow$  iodine. On the other hand, the polarising capacity of the cations diminishes with their volume *i.e.*, in the order  $\text{H} \rightarrow \text{Na} \rightarrow \text{K}$  etc.

The two extreme cases of  $\text{HClBr}_2$  and  $\text{HI}_3$  can now be represented by the following models:

*Ionic\_Radius.*



In I the replacement of  $H^+$  by  $Na^+$  or  $K^+$  of larger volume will naturally increase the stability of  $ClBr_2$  ions, whereas in II such replacement will diminish the stability of  $I'_3$  to a certain extent as the polarising power of cation diminishes. This also accounts for the higher values of equilibrium constants with larger halogen molecules and ions, which are more easily polarisable. In I the  $Cl^-$  ion is not appreciably polarised on account of its smaller volume and greater electron-affinity.

The cases of strontium and barium were not considered, for in their cases the influence of the  $SrCl$  or  $BaCl$  ion besides  $Sr$  or  $Ba$  ion complicates the matter. Moreover, the values of the equilibrium constants obtained in their cases are not accurate but only approximate.

#### SUMMARY.

By means of the freezing point depressions, the formation of polyhalides of the metals of the alkali and the alkaline earths have been confirmed and their dissociation constants determined at their freezing points. From the dissociation constants at the freezing points and from those at other temperatures determined by different investigators, their heats of formation have also been calculated. The following table gives the values of the dissociation constants and the heat of formation of the complexes:

	$NaClBr_2$	$KClBr_2$	$Sr_{\frac{1}{2}}ClBr_2$	$Ba_{\frac{1}{2}}ClBr_2$	$NaBr_3$	$KBr_3$	$Sr_{\frac{1}{2}}Br_3$	$Ba_{\frac{1}{2}}Br_3$
Dissociation constant	0.1769	0.174	0.092	0.077	0.0441	0.0437	0.016	0.014
Heat of formation (calories)	...	798	...	...	1917	1976	...	...

The divergence in the values of the equilibrium constants for any complex polyhalide ion with different cations is attributed to the electrostatic forces operating between the cation, the halogen ion and the halogen molecule.

My grateful thanks are due to Prof. P. R. Ray of the University College of Science and Prof. A. Maitra of the Presidency College for the kind interest in the work.

# Solubilities of Weak Acids in Salts of Weak Acids at Very High Concentrations.

By S. S. DOOSAJ AND W. V. BHAGWAT.

Philip (*J. Chem. Soc.*, 1905, **87**, 897) and Philip and Garner (*ibid.*, 1909, **95** 1466) have determined the solubilities of sparingly soluble acids in solutions of sodium salts of weak acids, but the range of the concentrations of sodium salt, they have investigated, is very small and that too very limited. In this paper, we have extended this work and have determined the solubilities of weak acids in very high concentrations of sodium salts of weak acids as well as for very low concentrations of these salts.

Our results of the solubilities are recorded below.

TABLE I.

*Solubility of benzoic acid.*

(a) *In sodium formate* Temp., 30°.

Conc , g./litre.			
Sodium formate.	Benzoic acid.	Sodium formate.	Benzoic acid.
0	4.033	28.6366	10.920
4.0541	6.339	42.9536	12.297
6.0662	6.964	64.0178	16.346
12.1724	8.404	112.0237	17.835
21.4768	9.638	168.0356	20.325

(b) *In sodium acetate. Temp., 80°.*

Conc , g /litre.

Sodium acetate.	Benzoic acid.	Sodium acetate.	Benzoic acid.
	4.033	27.3110	17.72
2.2322	5.750	33.6607	19.56
4.4643	7.484	46.4287	23.10
8.9286	10.00	58.0359	25.92
11.0544	11.09	67.3214	27.57
14.5099	12.33	100.9822	33.61
23.7605	16.17	134.6428	38.64
		201.0644	48.17

(c) *In sodium salicylate.*

Sodium salicylate.	Benzoic acid.	Sodium salicylate.	Benzoic acid.
0	4.033	73.0209	7.213
9.4220	4.174	97.3612	10.17
13.9087	4.252	146.0418	13.73
26.5580	5.029	194.7224	22.03
46.6806	5.759	242.0836	33.72
58.4167	6.624		

(d) *In sodium citrate.*

Sodium citrate.	Benzoic acid.	Sodium citrate.	Benzoic acid.
0	4.033	33.2951	19.24
5.8701	7.509	55.4918	25.03
7.9274	8.794	83.2377	30.20
15.1341	12.51	110.9836	34.03
27.7449	17.29	116.4754	39.25

TABLE II.

*Solubility of salicylic acid.*(a) *In sodium formate.* Temp., 30°.

Conc , g./litre.

Sodium formate.	Salicylic acid.	Sodium formate.	Salicylic acid.
0	2.743	33.2340	26.36
4.6456	8.624	36.0035	27.07
6.8578	10.35	48.0047	32.02
9.0003	12.08	72.0071	39.87
13.0022	15.15	144.0142	63.66
24.0024	21.04		

(b) *In sodium acetate.*

Sodium acetate.	Salicylic acid.	Sodium acetate.	Salicylic acid.
0	2.713	36.4989	31.06
2.3547	4.828	43.7986	36.22
3.5322	6.026	72.9977	57.25
7.0643	9.123	109.4966	77.43
10.4281	11.73	218.9932	147.20
19.9027	19.32		

(c) *In sodium citrate.*

Sodium citrate.	Salicylic acid.	Sodium citrate.	Salicylic acid.
0	2.743	33.2951	29.73
5.3701	7.875	55.4918	43.17
7.924	10.26	83.2377	57.15
15.1818	15.92	110.9836	71.91
27.7459	24.94	156.4754	90.78

(d) *In sodium benzoate.* Temp., 14·5°

Conc., g./litre.

Sodium benzoate.	Salicylic acid.	Sodium benzoate.	Salicylic acid.
0	1·667	34·6121	4·189
1·7306	2·427	57·6869	4·436
3·4612	3·393	86·5303	4·285
6·9224	3·829	115·3737	4·513
17·3061	4·171	173·0606	5·460

(e) *In sodium chloride.* Temp., 25°.

Sodium chloride.	Salicylic acid.	Sodium chloride.	Salicylic acid.
0	2·478	19·60	2·075
1·176	2·229	29·40	2·000
5·88	2·219	39·20	1·901
11·76	2·150	58·80	1·719
14·70	2·125		

TABLE IV.

*Solubility of cinnamic acid.*(a) *In sodium acetate.* Temp., 30°.

Conc., g./litre.

Sodium acetate.	Cinnamic acid.	Sodium acetate.	Cinnamic acid.
0	0·6937	36·4989	6·563
2·3574	1·763	43·7986	7·224
3·5322	2·334	72·9977	9·162
7·0643	2·907	109·4966	11·10
10·4281	3·525	218·9932	18·41
19·9067	4·825		

(b) *In sodium citrate.* Temp., 30°.

Conc., g./litre.

Sodium citrate.	Cinnamic acid.	Sodium citrate.	Cinnamic acid.
0	0.6937	33.2951	9.104
5.3701	3.469	55.1918	11.75
7.9274	4.317	83.2377	12.79
15.1341	6.322	110.9836	13.69
27.7459	8.486	166.1754	14.49

(c) *In sodium benzoate.* Temp., 16.3°.

Sodium benzoate	Cinnamic acid	Sodium benzoate.	Cinnamic acid.
0	0.3914	31.6121	2.997
1.7306	0.7827	57.1868	4.212
3.4612	1.021	86.5303	5.121
6.9224	1.393	115.3737	5.571
17.3061	2.069		

TABLE IV.

*Solubility of succinic acid.*(a) *In sodium salicylate.* Temp., 14.3°.

Conc., g./litre.

Sodium Salicylate.	Succinic acid..	Sodium salicylate.	Succinic acid.
0	50.23	81.0067	62.94
11.5809	59.00	121.6	93.71
22.1091	63.84	162.1333	97.79
40.5333	70.98	243.2	96.80

(b) *In sodium chloride.* Temp., 25°:

Conc , g./litre

Sodium chloride.	Succinic acid.	Sodium chloride.	Succinic acid.
0	70.03	313.2777	22.74
17.7001	74.85	316.0748	10.00
35.4003	68.55	319.0124	4.513
44.2505	66.51	321.8218	3.619
118.0013	52.25	327.8713	3.004
177.0019	42.27	333.9658	2.015
221.2523	36.03	347.0611	1.038
295.0031	26.52	351.0038	0.5224

## DISCUSSION.

(a) From our experimental results on solubilities it is observed that the solubility of a stronger acid is greater than that of a weaker acid for the same concentration of a sodium salt. It will be seen from the results that the solubility of these acids in pure water at 80° is of the same order of magnitude. But when we consider their solubilities in various concentrations of sodium salts such as sodium formate, sodium acetate and sodium citrate, the solubility of the stronger salicylic acid rapidly increases and is always greater than those of the weaker benzoic and cinnamic acids, although in pure water the solubility of benzoic acid is greater than that of salicylic acid.

(b) When we consider the solubilities of cinnamic and salicylic acids, we find that the solubility of salicylic acid increases more rapidly with the concentration of sodium benzoate than that of cinnamic acid for very low concentrations. When, however, the concentration of sodium benzoate increases, the solubility of cinnamic acid increases with the same rate, although the solubility of salicylic acid increases very slowly and that of the cinnamic acid finally exceeds the solubility of salicylic acid.

(c) The values for the solubility of succinic acid obtained in various concentrations of sodium salicylate are still more striking. The benzoic and succinic acids are more or less equally strong and it would, therefore, appear that the increase should practically be the same in both the cases. It is, however, observed that the increase



in solubility for the same concentration of sodium salicylate is much greater for succinic acid than for benzoic acid. When however the concentration of sodium salicylate exceeds 1M, the solubility of succinic acid instead of increasing with the concentration goes on decreasing, first gradually, and then rather rapidly.

(d) When the solubility of salicylic acid in sodium chloride is considered, the solubility falls first very rapidly with the concentration of sodium chloride and then very slowly. With succinic acid, the solubility increases for very low concentrations of sodium chloride and then gradually decreases.

It is clear from the above observations that the dibasic succinic acid behaves differently from the monobasic acids. Moreover, it should be observed from (b) that salicylic acid also slightly deviates from the general rule. Thus it appears that the increase in solubility of weak acids in their sodium salts is governed not only by their dissociation constants but also influenced by the basicity of the acid; this increase also depends on whether the acid is a normal or hydroxy acid.

If we compare the solubility of the same acid in various salts, it is observed that the solubility is greater and increases more rapidly in the salt of a weaker than in that of a stronger acid of the same concentration.

An interesting relation is observed when we study the solubilities of benzoic, salicylic and cinnamic acids in sodium citrate. Although citric acid is stronger than formic acid, yet the solubility of salicylic acid is much greater in sodium citrate than in sodium formate. Similarly the solubility of benzoic acid is much greater in sodium citrate than in sodium formate of the same concentration. The solubility of salicylic acid is more or less the same in sodium citrate and sodium acetate when the concentration of sodium salt is low, although citric acid is much stronger than acetic acid. At higher concentrations of the salts, the solubility of salicylic acid is much less in citrate than in acetate.

The solubilities of benzoic and cinnamic acids in the above two salts show a peculiar behaviour. For low concentrations of the salts, the solubilities of these acids are greater in sodium citrate than in sodium acetate, although acetic acid is a much weaker acid than citric acid, but with increase in concentration, the solubilities of cinnamic and benzoic acids are now less in sodium citrate than in sodium acetate of the same concentration. The solubility of salicylic

acid at low concentration is the same in sodium citrate, and sodium acetate ; it is greater in case of benzoic acid in sodium citrate and this variation is still greater in case of cinnamic acid. Thus citrate shows a peculiar behaviour.

In case of sodium formate and citrate, it will be seen that the rate of increase in the solubility of salicylic acid in sodium citrate is rapidly falling and if sufficiently high concentrations are taken, the solubility of salicylic acid may become less in sodium citrate than in sodium formate as expected on the basis of the strength of the acids from which these salts are prepared.

The behaviour of sodium salicylate is rather striking ; salicylic acid is stronger than formic acid and it is expected that the solubility of a dissolved acid should be less in sodium salicylate than in sodium formate and this conclusion is borne out only at the low concentrations of these salts. This behaviour is exactly the reverse of that of sodium citrate, in which the solubility at first increases and then diminishes at higher concentrations of sodium citrate.

The solubility of the weak acid instead of increasing on addition of a salt of a strong acid actually falls. Thus the solubilities of salicylic and succinic acids are less in sodium chloride than in pure water.

#### SUMMARY

(1) Solubilities of benzoic, salicylic, cinnamic, and succinic acids in sodium formate, sodium acetate, sodium salicylate, sodium citrate, sodium benzoate and sodium chloride have been determined over a very wide range of concentrations.

(2) The experimental results with solubilities show that the solubility of a weak acid in sodium salt of a weak acid depends on the strength of the acid used. Thus when we are considering the solubilities of various acids in the same salt, generally the stronger acid is more soluble but the solubility is also influenced by the basicity and the nature of the acids. Thus the solubilities show deviation from the general rule in the case of succinic acid which is dibasic and in case of salicylic acid, which is a hydroxy acid.

(3) When the solubilities of weak acids in salts of very strong acids are considered, it is found that the solubility in the salt solution is less than that in pure water and decreases with the increase in concentration of sodium salt. Thus sodium chloride shows this behaviour with salicylic and succinic acids.

# **Adsorption of Sodium Linoleate in Preference to that of Sodium Oleate on the Surface of Nickel and Copper.**

By B. S. SRIKANTAN.

Rideal (*Trans. Faraday Soc.*, 1923, 19, 90) from a study of the relative rates of hydrogenation of the salts of cinnamic and phenylpropionic acids in presence of colloidal palladium observed that at low concentrations of the sols, the phenylpropionate is hydrogenated twice as fast as the cinnamate. He suggests that, it is not due to preferential adsorption of the more unsaturated salt, but that the salts are not desorbed from the surface till completely saturated and that the phenylpropionate takes up two hydrogen molecules from palladium in the same time as the cinnamate takes up one. But most of the work on hydrogenation of oils involves the possibility of preferential hydrogenation of the more unsaturated glycerides (Moore, Richter and van Arsdel, *Ind. Eng. Chem.*, 1917, 9, 451; Richardson, Knuth and Milligave, *Amer. Chem. Soc.*, Sept. Meeting, 1923).

The present investigation was undertaken with the object of studying the effect of double bonds in adsorption processes at catalyst surfaces. The sodium salts of oleic and linoleic acids were chosen for study. The catalysts used were copper and nickel. If, (as is usually assumed) straight-chain fatty acids do not lie flat on the surface but stand upright, being adsorbed by the end radicle like  $-\text{COOH}$  group, one need not expect preferential adsorption; but if the molecules lie flat being multiply adsorbed through the agency of double bonds (Burk, *J. Phys. Chem.*, 1926, 30, 1134), then one could account for preferential adsorption of the substance having greater number of double bonds over the other with a smaller number of double bonds.

## **EXPERIMENTAL.**

**Preparation of soap.** :—The soaps were prepared by the methods of McBain. Alcoholic solution of sodium hydroxide was added to alcoholic solutions of the acids till the acids were neutralised. The soaps were washed several times with alcohol, and dried in a vacuum desiccator. The sample of sodium oleate was perfectly white and melted

between 233-34°. The linoleate was soxhleted with petrol and repeatedly, crystallised from methyl alcohol and dried (m. p. 244°, decomp.).

*Preparation of nickel.*—Nickel carbonate was precipitated by the action of a cold solution of sodium carbonate saturated with carbon dioxide on a saturated solution of nickel nitrate. It was washed free from nitrate and dried at 100°, reduced at 320° for 3 hours in a current of dry electrolytic hydrogen, free from oxygen. Nickel reduced below 270° was found to be pyrophoric and could not be worked with. Nickel reduced at 320° was stable and was always kept in a vacuum desiccator except when taken out for weighing.

*Preparation of copper.*—Dark-red copper oxide was precipitated from a concentrated solution of copper sulphate by a concentrated solution of sodium hydroxide. It was washed thoroughly with distilled water till free from traces of alkali. The filtrate cake was dried at 100°. The oxide when reduced at 200° was very pyrophoric. So it was reduced at 320° by a slow current of dry electrolytic hydrogen, free from oxygen. The copper was orange-red in colour, made into uniform powder and kept in a desiccator.

*Method of work.*—The soap solutions employed were between 0.1-0.5%. The method of estimating the concentration of soaps in solution before and after adsorption was by the use of Donnan's drop pipette (*Z. physikal. Chem.*, 1899, 31, 42). The number of drops in a known volume of the solution of various concentrations was first noted. The change in the drop number with concentrations at 30° is given in Table I. The pipette was always cleaned and dried before each observation.

TABLE I.

		Temperature 30°						
% of soap	...	0.000	0.050	0.100	0.200	0.250	0.400	0.500
Drop. Nos. {	Sod. oleate ...	173	303	378	422	429	446	455
	Sod. linoleate ...	173	236	277	330	347	358	368

Weighed quantities of the catalysts in contact with 50 c.c. of soap solutions of different concentrations in well stoppered bottles were kept in an accurately controlled thermostat at 30° for a day. The drop numbers of solutions after adsorption were found out. The concentrations of the soap solutions after adsorption were read off from the

drop number-concentration graph drawn with the help of Table I. The value of the concentrations of solutions before and after adsorption gave the figures for the amount of soap adsorbed from 100 c.c. of solution. Table II gives the summary of the results.

TABLE II.

Nickel.

Wt. of catalyst.	Soap conc.	Drop No. after adsorption		Amount adsorbed from 100 c.c.	
		Oleate.	Linoleate.	Oleate.	Linoleate.
0.5 g.	0.2 %	418	365	0.0025	0.0574
	0.4	445	343	0.0100	0.1624
	0.5	450	336	0.0574	0.2850
1.0	0.1	357	267	0.0230	0.0125
	0.2	411	301	0.0324	0.0625
	0.4	442	335	0.0500	0.1874
	0.5	447	324	0.0900	0.3144
2.5	0.1	255	261	0.0700	0.0220
	0.2	372	293	0.1074	0.0774
	0.4	435	322	0.1100	0.2174

Copper.

0.5	0.2	412	281	0.0300	0.0500
	0.4	439	304	0.0744	0.2550
	0.5	448	325	0.0800	0.3100
1.0	0.2	408	266	0.0400	0.1140
	0.5	447	324	0.0800	0.3124
2.5	0.4	431	303	0.1400	0.2575
	0.5	443	222	0.1374	0.3174

The results are of a preliminary nature. However, it appears that for concentrations of 0.2 % and more, the linoleate is adsorbed more in preference to the oleate. A detailed investigation at low concentrations would be interesting.



# **Studies in the Protective Action of Colloids. Part I.**

## **Ionic Adsorption in the Coagulation of Protected Sols.**

BY SHRIDHAR SARVOTTAM JOSHI AND A. JOGA RAO.

A review of the literature on the subject showed that very little quantitative information is available on the ionic adsorption by a sol when coagulated in presence of a protecting agent. The following experiments were carried out with colloidal arsenious sulphide protected by variously concentrated solutions of gelatine, sodium oleate, and starch, using solutions of ferric chloride, barium chloride and hydrochloric acid as coagulators.

### **EXPERIMENTAL.**

By preliminary experiments, the range of the proper concentrations of the solutions of the protectors was determined, so that for these values, the coagulation of a given concentration of the sol due to any of the variously concentrated solutions of the electrolytes used was complete within at least 48 hours. The following procedure was adopted for measuring the ionic adsorption: 25 c.c. of the sol were taken into a number of 100 c.c. flasks which were previously well-cleaned, steamed and dried. In one of these flasks 25 c.c. of distilled water were added to the sol; in the rest, the same volume of the protector solutions of increasing concentrations were added. Then in every one of these, 50 c.c. of the electrolyte solution of a known concentration were carefully added, the mixture was once shaken, and allowed to stand for subsequent analysis. The concentration of the electrolyte was such as to produce complete coagulation in all the systems within the period mentioned above. The amount of ionic adsorption was measured by withdrawing a known volume from the clear supernatant layers of the flocculated sol.

The results in Tables I, II and III show the variation of the amount of ionic adsorption, when the concentration of the protector solution, *vis.*, gelatine, was varied. Coagulations were produced by different concentrations of barium chloride solutions. The amount of barium adsorbed by the coagulum was estimated as barium sulphate by the familiar gravimetric method. Blank experiments in which arsenious

sulphide was not added, showed that any inaccuracy involved due to incomplete precipitation of barium sulphate due to the presence of gelatine added, was of the order of 0.1 per cent.

$a$ , denotes the original amount of barium present in the system before coagulation and is expressed as grams of  $\text{BaSO}_4$ . The data under  $b$ , give the amount of the barium expressed in the same way after coagulation. The data under,  $(a-b)$ , denote therefore the amount of barium adsorbed by the coagulum. The data in the last column express  $(a-b)$ , as millimoles of barium. In the first column, under  $p$ , are given the percentage concentrations of the protecting solutions employed.

TABLE I.

*Sol protected by gelatine*

Conc. of the  $\text{BaCl}_2$  solution =  $N/20$ . Conc. of the  $\text{As}_2\text{S}_3$  sol = 4 g. of  $\text{As}_2\text{O}_3$  per litre.  $a = 0.3065$  g.

$p$ .	$b$ .	$a-b$ .	Adsorption of Ba in m. mols.
0.0 %	0.2901	0.0161	0.0694
0.0031	0.2870	0.0195	0.0835
0.0062	0.2876	0.0189	0.0809
0.0125	0.2916	0.0149	0.0638
0.0250	0.2912	0.0153	0.0656
0.0500	0.2892	0.0173	0.0741
0.1000	0.2840	0.0225	0.0964
0.2000	Only partial coagulation.		

TABLE II.

*Sol protected by gelatine.*

Conc. of  $\text{BaCl}_2$  solution =  $N/20$ . Conc. of the  $\text{As}_2\text{S}_3$  sol = 2 g. of  $\text{As}_2\text{O}_3$  per litre.  $a = 0.2976$  g.

$p$ .	$b$ .	$a-b$ .	Adsorption of Ba in m. mols.
0.0000	0.2888	0.0088	0.0377
0.0016	0.2864	0.0112	0.0480
0.0031	0.2966	0.0010	0.0043
0.0063	0.2904	0.0072	0.0308
0.0125	0.2936	0.0040	0.0171
0.0250	0.2852	0.0124	0.0531
0.0500	Much turbidity, but no settling.		
0.1000	Not much turbidity.		



TABLE III.

*Sol protected by gelatine.*

Conc. of  $\text{BaCl}_2$  solution =  $N/4$ . Conc. of the  $\text{As}_2\text{S}_3$  sol = 1.8 g. of  $\text{As}_2\text{O}_3$  per litre.  $a = 1.4560$  g.

$p$ .	$b$ .	$a - b$ .	Adsorption of Ba in m. mols.
0.0000	1.4440	0.0120	0.0514
0.0012	1.4480	0.0080	0.0343
0.0025	1.4412	0.0148	0.0634
0.0050	1.4492	0.0068	0.0291
0.0100	1.4444	0.0116	0.0497
0.0200	1.4434	0.0126	0.0539
0.0300	1.4416	0.0144	0.0616
0.0400	} Only partial coagulation.		
0.0500			
0.1000			

The results in Tables IV, V, VI relate the amount of ionic adsorption at different concentrations of gelatine solution when ferric chloride was the coagulant. The amounts of the ferric ion adsorbed were estimated volumetrically by reduction with stannous chloride and titrating against standard dichromate solution.  $a$ ,  $b$ ,  $(a - b)$  have their previous significance; they are expressed as c.c. of normal dichromate solution equivalent to the corresponding ferric chloride solutions.

TABLE IV.

*Sol protected by gelatine.*

Conc. of  $\text{FeCl}_3$  solution employed =  $N/1$ . Conc. of the  $\text{As}_2\text{S}_3$  = 4 g. of  $\text{As}_2\text{O}_3$  per litre.  $a = 102$  (0.5187 c.c.)

$p$ .	$b$ .	$a - b$ .	Adsorption of Fe in m. mols.
0.000	53	49	25.41
0.015	52	50	25.94
0.031	53	49	25.41
0.062	52.5	49.5	25.67
0.125	52.25	49.75	25.81
0.250	53.25	48.75	25.31
0.500	51.75	50.25	26.10

TABLE V.

*Sol protected by gelatine.*

Conc. of  $\text{FeCl}_3$  solution =  $N/4$ . Conc. of the  $\text{As}_2\text{S}_3$  sol = 4 g. per litre.  $a = 26.4$  (0.5187 c.c.).

$p$ .	$b$ .	$a - b$ .	Adsorption of Fe in m. mols.
0.000	14	12.4	6.439
0.015	14	12.4	6.439
0.031	13.25	13.15	6.828
0.062	14.25	12.15	6.275
0.125	13.00	13.4	6.955
0.250	13.50	12.9	6.697
0.500	Incomplete coagulation.		

TABLE VI.

*Sol protected by gelatine.*

Conc. of the  $\text{FeCl}_3$  solution =  $N/4.5$ . Conc. of the  $\text{As}_2\text{S}_3$  sol = 4 g. per litre.  $a = 44.96$  (0.2559 c.c.).

$p$ .	$b$ .	$a - b$ .	Adsorption of Fe in m. mols.
0.000	20.45	24.51	6.270
0.006	20.20	24.76	6.345
0.010	20.25	24.71	6.338
0.020	20.40	24.56	6.295
0.025	20.90	24.06	6.141
0.050	20.50	24.46	6.269
0.100	20.15	24.81	6.359
0.140	19.70	25.26	6.474
0.200	Incomplete coagulation.		

The results in Tables VII and VIII show the variation of the ionic adsorption when barium chloride and hydrochloric acid respectively were used, with increasing concentrations of sodium oleate solutions. The adsorption of the barium ion was estimated as in the previous cases. Adsorption in coagulations with hydrochloric acid was estimated by titration with standard alkali solution. Due correction was applied in each case for the characteristic alkalinity of the sodium oleate solutions ;  $p$ ,  $a$ ,  $b$ ,  $(a-b)$  have their usual significance.

TABLE VII.

*Sol protected by sodium oleate.*

Conc. of the  $\text{BaCl}_2$  solution =  $N/2$ . Conc. of the  $\text{As}_2\text{S}_3$  sol = 4 g of  $\text{As}_2\text{O}_3$  per litre  $a = 2.9692$  g

$p$	$b$	$a-b$	Adsorption of Ba in m. mole.
0.000	2.9512	0.0180	0.077
0.003	2.9472	0.0220	0.095
0.006	2.9392	0.0300	0.129
0.012	2.9440	0.0252	0.108
0.015	2.9432	0.0260	0.111
0.018	2.9392	0.0300	0.129
0.024	2.9094	0.0598	0.159
0.030	2.9360	0.0332	0.142
0.037	2.9334	0.0358	0.153
0.045	2.9324	0.0368	0.158
0.060	2.9308	0.0384	0.165
0.075	2.9332	0.0360	0.154

In Table VIII,  $a$  denotes the original amount of the hydrochloric acid present in the system before coagulation, expressed as c.c. of standard alkali solution.  $b$ ,  $(a-b)$  are expressed in the same way as previously ;  $p$  denotes the percentage concentration of the protective agent solution employed. In this set, however, instead of keeping the volumes of the protecting solution and the coagulant, 25 c. c. and 50 c. c. respectively, they were reversed.

TABLE VIII.

*Sol protected by sodium oleate.*

Conc. of HCl solution employed =  $N/10$ . Conc. of the  $As_2S_3$  sol = 4 g. of  $As_2O_3$  per litre.  $a = 152.3$  c. c.

$p$ .	$b$ .	$a-b$ .	Adsorption of HCl in m. mols.
0.00	151.40 c. c.	0.90 c. c.	0.0686
0.05	150.09	2.20	0.1680
0.10	149.79	2.51	0.1915
0.20	149.51	2.76	0.2107
0.25	149.71	2.59	0.1973
0.30	148.16	4.14	0.3152
0.40	146.99	5.31	0.4106
0.50	146.62	5.68	0.4326

Table IX gives results for the barium ionic adsorptions when starch solutions were employed as protectors. The volumes of the sol, protector, and coagulant, were the same as in the first seven sets, viz., 25 c.c., 25 c.c., 50 c.c. respectively.

TABLE IX.

*Sol protected by starch.*

Conc. of  $BaCl_2$  solution employed =  $N/2$ . Conc. of the  $As_2S_3$  sol = 6 g. of  $As_2O_3$  per litre.  $a = 2.9541$  g.

$p$ .	$b$ .	$a-b$ .	Adsorption of Ba in m. mols.
0.00	2.8724	0.0817	0.350
0.02	2.8698	0.0843	0.361
0.04	2.8672	0.0869	0.372
0.06	2.8664	0.0877	0.376
0.07	2.8761	0.0780	0.384
0.08	2.8910	0.0631	0.270
0.09	2.8848	0.0693	0.297
0.10	2.8788	0.0753	0.323
0.11	2.8729	0.0812	0.348
0.12	2.8660	0.0881	0.378
0.14	2.8726	0.0815	0.349
0.16	2.8770	0.0771	0.330

Next, the adsorption of barium ions by the simple, unprotected arsenious sulphide sol at various dilutions was determined, and the results are given in Table X. Sols of various dilutions were obtained by diluting 1,  $2\frac{1}{2}$ , 5 c. c. etc., of the stock sol to 25 c. c. Into each of these, 25 c. c. of barium chloride solutions were added, and the adsorption of barium ions was estimated after 24 hours. The data in the first column, denoted by *S*, indicate the number of c. c. of the stock  $\text{As}_2\text{S}_3$  sol diluted to 25 c. c.

TABLE X.

*No protector used*

Conc. of  $\text{BaCl}_2$  solution =  $N/3$ . Conc of the  $\text{As}_2\text{S}_3$  sol = 2 g. of  $\text{As}_2\text{O}_3$  per litre.  $a = 0.9946$  g.

<i>S</i> .	<i>b</i> .	<i>a-b</i> .	Adsorption of Ba in m. mols.
1 c. c. diluted to 25 c. c.	0.9882	0.0664	0.0274
2.5 "	0.9822	0.0124	0.0524
5 "	0.9846	0.0100	0.0428
7 "	0.9812	0.0134	0.0574
10 "	0.9776	0.0170	0.0728
12 "	0.9716	0.0230	0.0885
14 "	0.9650	0.0266	0.1140
16 "	0.9642	0.0304	0.1302
20 "	0.9622	0.0324	0.1388
25 "	0.9582	0.0364	0.1560

In Table XI are given the results of the variation of the ionic adsorption with the concentration of the protective agent solution, when the arsenious sulphide sol was not present in the system. In each case, 25 c. c. of barium chloride solution were added to 25 c. c. of sodium oleate solution of known strength. The estimation of the adsorption of barium ions after coagulation was done as usual. The data under, *p*, give the percentage concentrations of the sodium oleate employed.

TABLE XI.

*Adsorption by sodium oleate only.*Conc. of  $\text{BaCl}_2$  solution =  $N/8$ .  $a = 0.9986$  g.

<i>p.</i>	<i>b.</i>	<i>a-b.</i>	Adsorption of Ba in m. mols.
0.004	0.9852	0.0084	0.036
0.010	0.9821	0.0112	0.048
0.020	0.9752	0.0184	0.079
0.040	0.9646	0.0290	0.124
0.060	0.9520	0.0416	0.178
0.080	0.9502	0.0344	0.147
0.100	0.9556	0.0380	0.163
0.200	0.9518	0.0418	0.178
0.400	0.9168	0.0768	0.329

The curves in Figs. 1—3 relate the amount of ionic adsorption with that of the protecting agent in the system; these curves numbered 1, 2,.....11 correspond to data in Tables I, II, III,.....XI respectively.

FIG. 1.

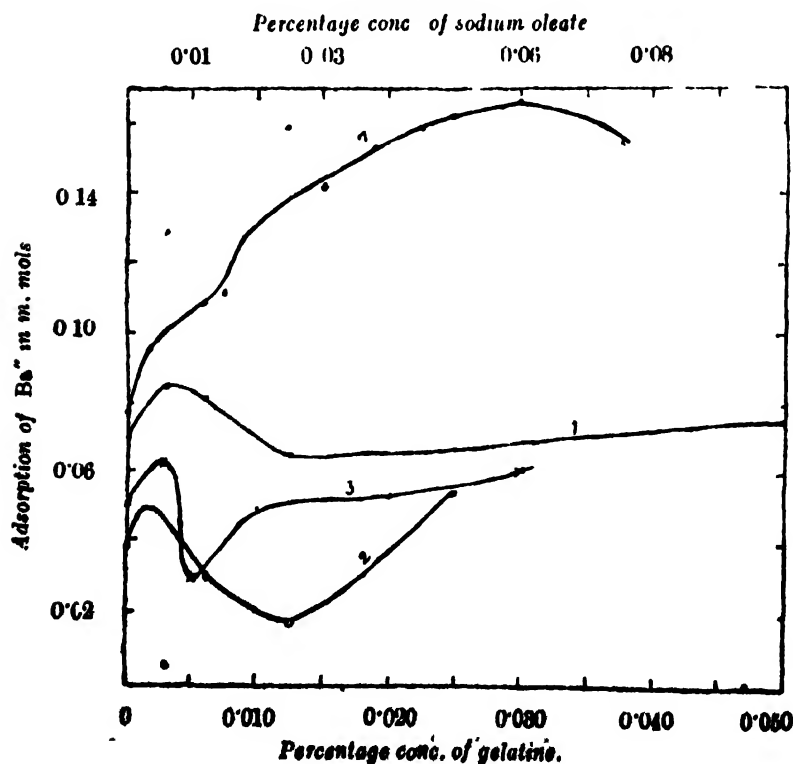


FIG. 2.

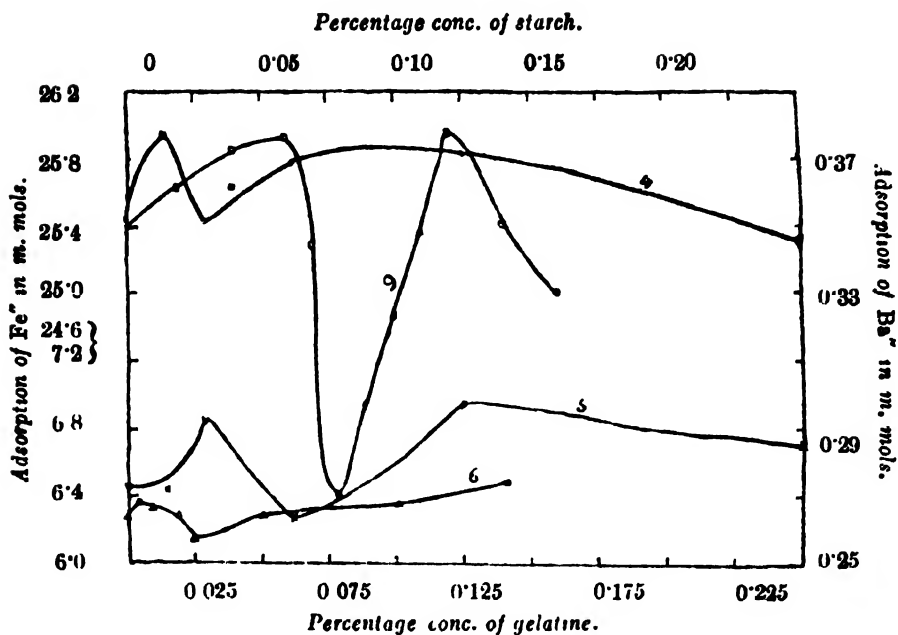
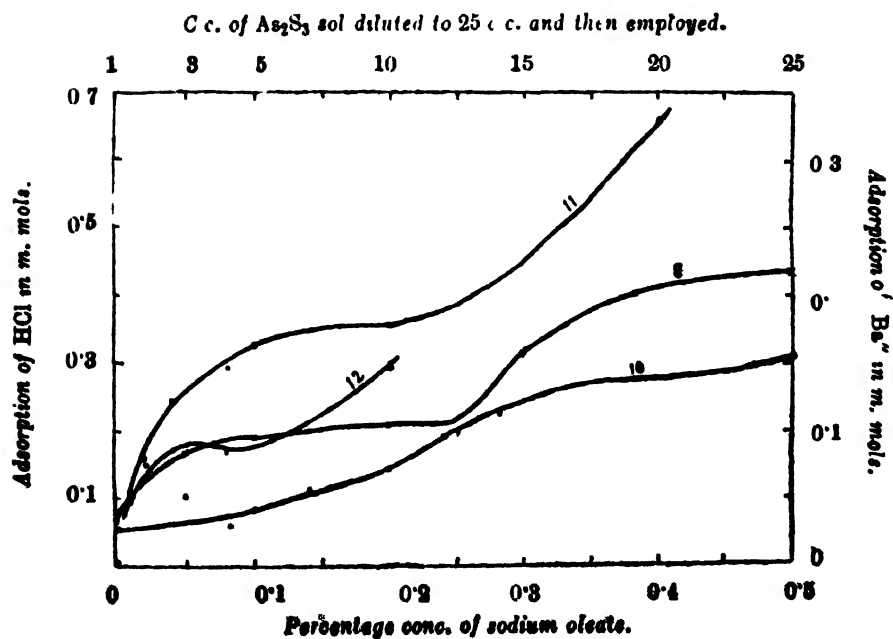


FIG. 3.



## DISCUSSION.

The results show that in the majority of cases for small proportions of the protector, adsorption of the coagulator increases by increasing the amount of the protector. It is, however, interesting to see in a number of cases that an increase in the proportion of the protector has led to a diminution of ionic adsorption. This is particularly well brought out, *e. g.*, by the minimum in curve 9, Fig. 2, showing the variable adsorption of barium as the proportion of the starch, introduced initially as a protector, is increased progressively. In this connection it is interesting to refer to the results of Chowdhury and Das (*J. Indian Chem. Soc.*, 1930, 7, 378) on the decolorisation of oils by mixed adsorbents, *viz.* alumina and bauxite, silica and bauxite. They found that the amount of the colouring matter removed, plotted against the proportion of one of the constituents of the adsorbing mixture, yields a curve with maxima and minima similar to those observed in the present work. Work of Chowdhury and Pal (*ibid.*, 1930, 7, 451) on the adsorption of benzol vapour by mixed adsorbents shows similar results. We are of opinion that the discontinuities like the ones mentioned above and observed by us indicate the formation of adsorption complexes between the added protector and the original colloid, with characteristic adsorption capacities. Results observed when ferric chloride was used as a coagulator are interesting (*cf.* Tables IV, V, VI). It is seen that the amount of adsorption is practically constant although the proportion of the protector has been varied, *e. g.*, in Table IV from 0.015 to 0.5 per cent. It is also remarkable that the electrolytic adsorption of the sol when protected by gelatine is approximately the same as that for the unprotected sol.

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## Studies in the Protective Action of Colloids. Part II.

By SHRIDHAR SARVOTTAM JOSHI AND A. JOGA RAO.

In Part I of this series (p. 237) a fixed quantity of the arsenious sulphide sol, protected by varying concentrations of a number of protecting agents, was coagulated by different electrolytes. It was found that the curves relating the amount of ionic adsorption with the corresponding concentration of the protector showed sharp discontinuities, which were attributed to the formation of adsorption complexes with specific adsorptive capacities. The following experiments were carried out in order to investigate if the above discontinuities were accompanied by a like change in two of the physical properties of the system, *viz.*, the viscosity and the turbidity, and their variation due to 'ageing'. The adsorption by the colloid of the protector itself also appeared to be a possible factor, and has been studied in the case of sodium oleate.

### EXPERIMENTAL.

25 C. c. of the arsenious sulphide sol were taken into each of a number of well cleaned 100 c. c. flasks. Into one of these, 25 c. c. of distilled water were added; in the rest the same volume of gelatine solutions of increasing concentrations (denoted by *p* in Tables I—IV), was added. The mixtures were then shaken, and their viscosities and turbidities determined. These measurements were again taken after the mixtures were allowed to stand (screened from light) for 30 hours.

The viscosity was measured by the method due to Scarpa (*Gazzetta*, 1920, **40**, 271; *cf.* also, Farrow, *J. Chem. Soc.*, 1912, **101**, 347). It consists in measuring the time of rise,  $t_1$  and of fall,  $t_2$ , for a certain volume of the liquid against a constant reduced pressure, and under a certain hydrostatic pressure of the liquid itself, respectively. The viscosity,  $\eta$ , is then given by,

$$\eta = \frac{k.t_1.t_2}{t_1 + t_2}$$

where  $k$  is a constant for the instrument used and can be evaluated by measuring  $t_1$  and  $t_2$  for a liquid whose viscosity is known, *e.g.*, water. The colloid solutions were allowed to attain the desired temperature by immersion in a thermostat for about half an hour. The thermostat temperature was kept constant within  $0.05^\circ$ . In Tables I—IV,  $p$  denotes the concentration of the gelatine solution; it was used as a protector in experiments to which Tables II, III, and IV refer. Table I gives  $\eta$ , for different values of  $p$ , for gelatine solutions only. Table II shows the viscosities of the gelatine-protected sols observed immediately after the addition of the protecting agent, for different values of  $p$ . Data in Tables III and IV refer to two independent series of experiments in which  $\eta$  was observed 30 hours after mixing the gelatine solution with the colloid.

Turbidity was determined by means of an instrument of a Nephelometer type. It consists essentially of two tubes to hold the liquids to be examined, which are illuminated from below. The depths of the liquids as shown by separate indicators can be varied by a rack and pinion arrangement, and the beams emerging from the liquid columns matched by viewing through the eyepieces fitted on the tubes. The left hand tube was always filled with the arsenious sulphide sol diluted with an equal volume of water, the indicator being kept at a certain height. The other tube was filled with the liquid to be examined for turbidity. The height of the latter, as shown by the indicator, is varied till the beams emerging from the two tubes just matched. This measurement was repeated with at least two different heights of the indicator in the standard liquid. The difference between the two heights gave a measure of the turbidity relative to that of the liquid taken as the standard. Table V and curves 1 and 2, Fig. 2, give the results of these measurements immediately after the sol was mixed with gelatine solutions of varying concentrations. Turbidities were determined for the same mixtures after 24 hours, and the results obtained shown in Table VI, and by curves 3, 4 and 5 in Fig. 2.

Experiments were next made in order to obtain some idea of the adsorption by the colloid of the protecting substance used, *viz.*, sodium oleate. Surface tensions of differently concentrated solutions of sodium oleate were measured by means of a stalagmometer. The solutions were so dilute that the difference of their densities from that of water was found to be negligible. Surface tensions have been indicated therefore only by the drop numbers. The results are shown

by the curve 6 in Fig. 3. Mixtures were next prepared in which a constant volume of the sol was protected by an equal volume of sodium oleate solution of different concentrations. The mixtures were allowed to stand for 24 hours, and their drop numbers determined. These are shown under  $D$  in Table VII.  $a$  and  $a/2$  refer respectively to sodium oleate concentrations before and after mixing. Sodium oleate concentrations corresponding to the drop numbers,  $D$ , observed for the mixed solutions were next read off from curve 6 in Fig. 3 and are quoted under  $b$  in Table VII.  $(a/2 - b)$  was taken as a measure of the amount of sodium oleate removed from water due to its adsorption by the colloid. Curve 7 in Fig. 3 relates the amount of the above adsorption with the concentration of the protector.

TABLE I.

*Pure gelatine solutions.*

TABLE II.

*Colloid + gelatine solutions.  
η Observed soon after  
mixing.*

TABLE III.

*Colloid + gelatine solutions. η Observed 80 hours  
after mixing.*

TABLE IV.

P.	t <sub>1</sub> .	t <sub>2</sub> .	η.	t <sub>1</sub> .	t <sub>2</sub> .	η.	t <sub>1</sub> .	t <sub>2</sub> .	η.
0·000	6' 42·8	11' 37·4	0·894	6' 50·4	11' 44·8	0·908	6' 51·4	11' 84·8	0·905
0·001	6 45·0	11 39·6	0·902	6' 54·6	11 45·8	0·914	6 52·4	11 47·4	0·912
0·003	6 47·4	11 46·0	0·904	6' 56·0	11 50·4	0·918	6 52·2	11 48·6	0·912
0·006	6 58·4	11 53·6	0·937	6' 58·8	11 56·6	0·925	6 55·8	12 0 0	0·922
0·010	7 11·4	11 56·0	0·942	6' 59·0	12 4·0	0·929	6 53·6	11 55·4	0·918
0·015	7 15·2	12 22·8	0·961	6' 59·0	12 12·8	0·934	6 45·0	11 56·8	0·908
0·020	7 20·0	12 38·3	0·974	7' 0	12 15·0	0·936	6 45·0	12 0 0	0·909
0·030	7 37·4	13 4·4	1·011	7' 1·0	12 15·2	0·987	6 48·8	12 2 0	0·914
0·040	7 55·0	13 41·6	1·054	7' 7 0	12 35·0	0·950	6 55·0	12 3 0	0·923
0·050	8 11·4	14 16·8	1·088	7' 5·4	12 40·0	0·950	6 54·0	12 2 0	0·921
							...	...	...

TABLE V.

*Immediately after mixing.*

No.	Percentage of gelatine.	Left height in cm.	Right height in cm.	Relative turbidity.
-----	-------------------------------	--------------------------	---------------------------	------------------------

1	0.000	20	20	0
	"	30	30	0

2	0.001	20	19	1
	"	"	"	"

3	0.003			
	"	20	15	5
	"	30	20	10

4	0.006			
	"	20	12	8
	"	30	16	14

5	0.010			
	"	20	8	12
	"	30	10.5	19.5

6	0.015			
	"	20	6	14
	"	30	7	23

7	0.020			
	"	20	4.5	15.5
	"	30	6.0	24

8	0.030			
	"	20	4.5	15.5
	"	30	5.5	24.5

9	0.040			
	"	20	3.5	16.5
	"	30	4.5	25.5

10	0.060			
	"	20	3	17
	"	30		26

TABLE VI.

*After 24 hours.*

Left height in cm.	Right height in cm.	Relative turbidity.
--------------------------	---------------------------	------------------------

10	10	0
20	20	0
30	30	0

10	7	3
20	16.5	3.5
30	22	8

10	6	4
20	12.5	7.5
30	16	14

10	5	5
20	8	12
30	12	18

10	4	6
20	5.5	14.5
30	8	22

10	2.5	7.5
20	4.5	15.5
30	5.5	24.5

10	2	∞
20	3.5	16.5
30	5	25

10	2	8
20	3.5	16.5
30	5	25

10	1.5	8.5
20	2.5	17.5
30	3.5	26.5

10	1	9
20	2.5	17.5
30	3.5	26.5

TABLE VII.

<i>a.</i>	<i>a</i> / <i>2</i> .	<i>D.</i>	<i>b.</i>	$\frac{a}{2}-b.$
0.05	0.025	163	0.0155	0.0095
0.10	0.050	177	0.0165	0.0335
0.20	0.100	254	0.0180	0.0820
0.25	0.125	272	0.0200	0.1050
0.30	0.150	300	0.0263	0.1237
0.40	0.200	335	0.0350	0.1650

FIG. 1.

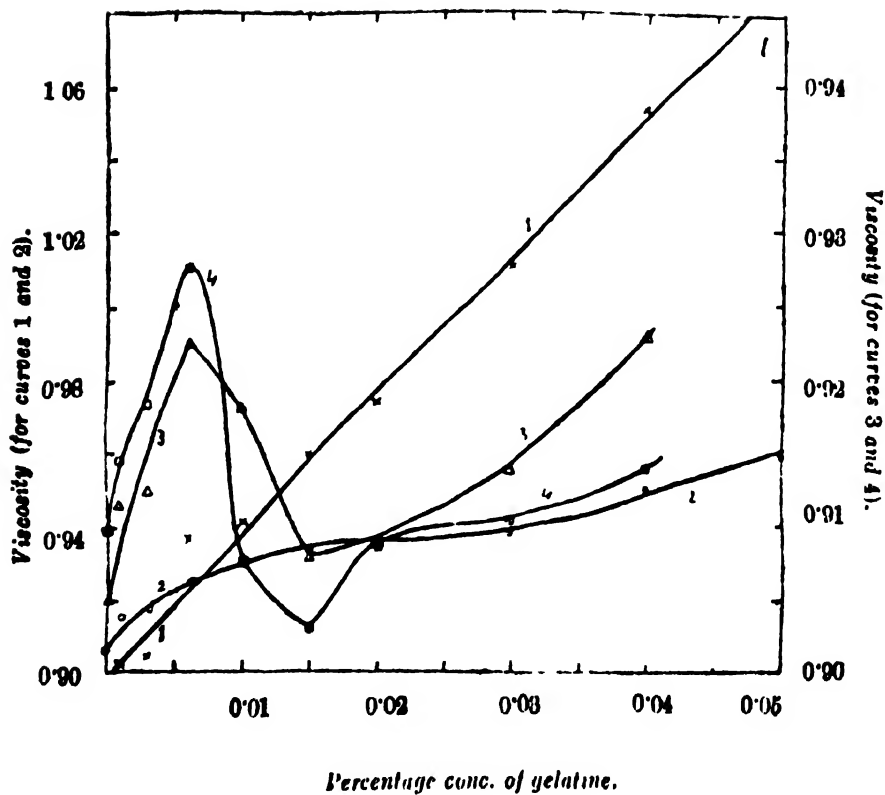


FIG. 2.

Turbidity observed soon after mixing. Curves 1 and 2 with the standard liquid at heights of 20 and 30 cm. respectively.

Turbidity observed 24 hours after mixing. Curves 3-5 with standard liquid at heights of 10, 20 and 30 cm. respectively.

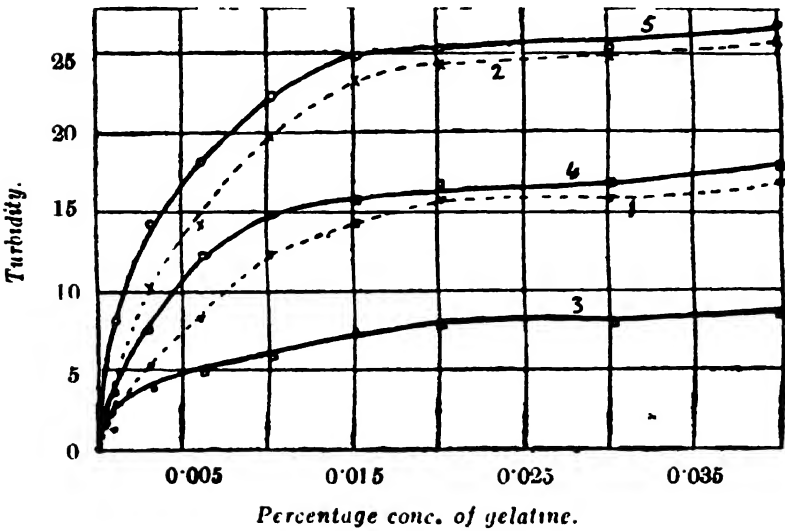
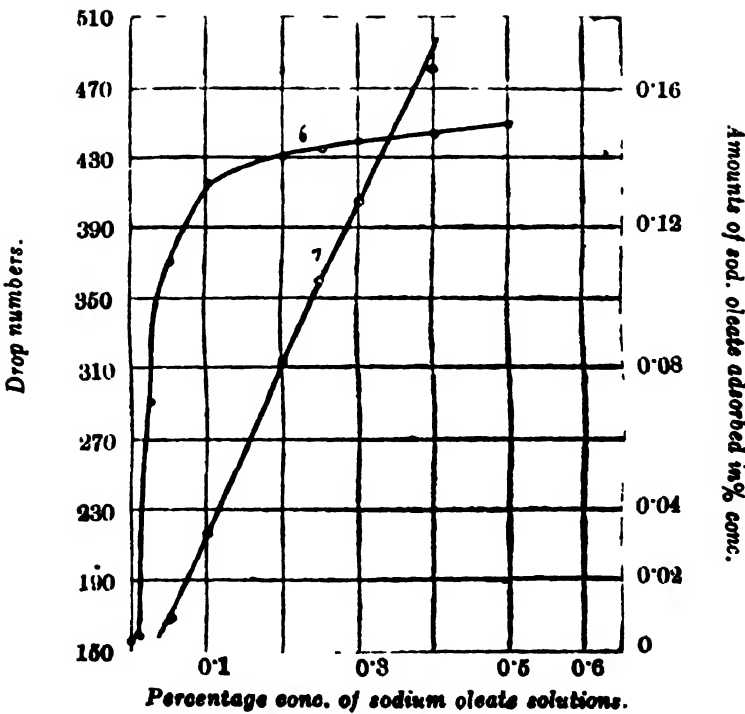


FIG. 3.



## DISCUSSION.

It is seen from curve 1, Fig. 1, that,  $\eta$ , the viscosity of gelatine solutions increases practically linearly by increasing  $p$ , its concentration. Similar results have been observed by Davis and Oakes, (*J. Amer. Chem. Soc.*, 1921, 43, 1526; *ibid.*, 1922, 44, 464). The  $\eta$ - $p$  relation is also a simple one for mixture of gelatine solutions with the colloid,  $\eta$  being determined soon after mixing (*cf.* curve 2, Fig. 1). Marked discontinuities, similar to those observed previously (Part I) in ionic adsorption-protector concentration curves, appeared when the protected sols were allowed to stand for a period of about 30 hours (curves 3 and 4). These two sets of results although not identical are sufficiently similar to show that the positions of discontinuity are more than mere accidental breaks due to experimental error. Indeed a lack of complete reproducibility of results within a given time period is well known in colloidal systems, and is to be attributed to the heterogeneity of the solutions, and the marked dependence of their properties on the manner of their preparation, especially in the case of lyophiles, although the same quantities of the materials are used. We are inclined, therefore, to consider the above discontinuities as indicative of (i) some kind of interaction between the protector and the colloid, (ii) some sudden changes in the nature and the size of particles of the dispersed phase, or (iii) what is more likely, due to the combined effect of (i) and (ii). Possibly these changes are amongst the main factors in the so-called 'ageing' phenomena, in which a time variation of some of the properties of colloids, notably of the viscosity, is observed. In this connection it is interesting to point out that the above changes in viscosity produced within only 30 hours are markedly greater than those found usually in the 'ageing' of simple sols, and might, therefore, be distinctive of only the protected systems.

It is important to note that the turbidity measurements show only a continuous increase with the concentration of the protector in every case. While the explanation of this result requires more detailed experimental work on protected sols, it may be perhaps permissible to point out one general result noted incidentally in the course of studies of the coagulation processes and using different methods of measuring the degree of coagulation which has been in progress for some time in these laboratories, that a given change in a colloid system does not reveal itself equally markedly in all its properties (*J. Indian Chem. Soc.*, 1981, 8, 11, 387; *ibid.*, 1982, 9, 157).



By comparing curves 4 and 5 with 1 and 2 in Fig. 2, it is seen that turbidity diminishes with ageing, and that this diminution is more appreciable at low proportions of the protector.

It is well known that one of the chief difficulties of interpreting results for protected systems in general, has been that no accurate method is available for the estimation of the adsorption of the protector. We have determined this for sodium oleate on the assumption that the difference in the surface tension of its solution when pure, and when mixed with the colloid is due entirely to its adsorption by the colloid ( $\frac{a}{2} - b$ , in Table VII). This is supported by the fact that the surface tension of the colloid solution used in the above experiments differed but little from that of pure water. The possible ascribability of the observed change of surface tension to alterations in the nature of the colloid particles in the system, besides that due to the factor assumed above, must be regarded as an open question. Our main assumption would appear, however, to be confirmed by the significant result (*cf.* curve 7, Fig. 3) that the amount of sodium oleate adsorbed increases practically linearly as its concentration is increased.

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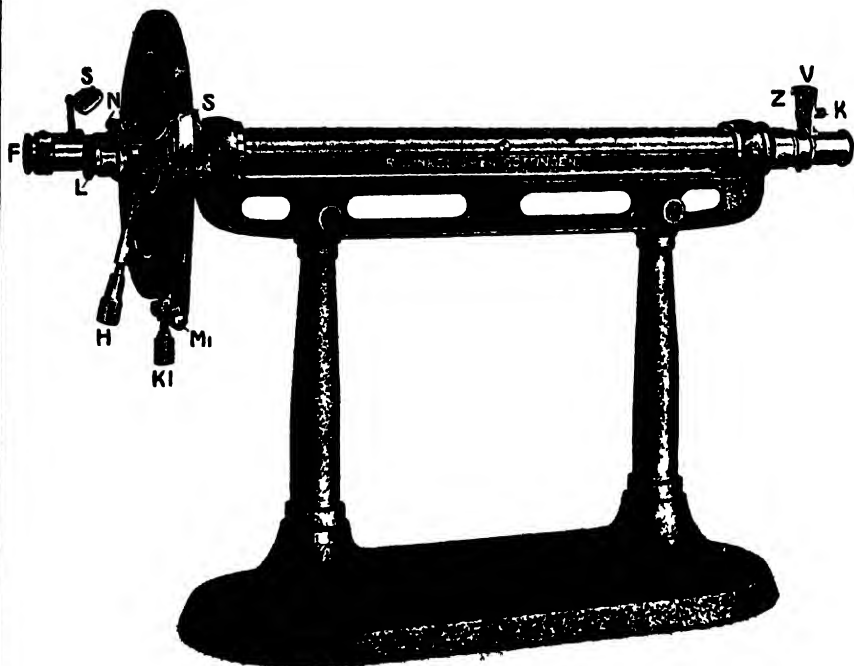
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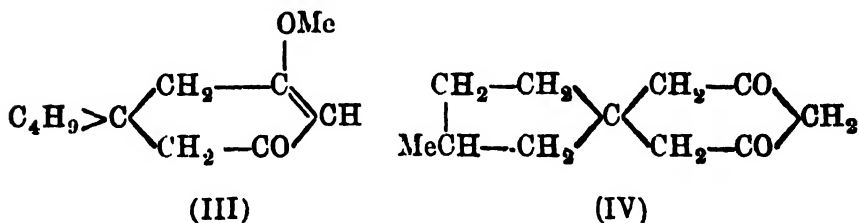


# The Chemistry of Alkylcyclopentanones. Part III.

## The Synthesis of 3'-Methylcyclopentane- spiro-cyclohexane-3 : 5-dione.

By RANCHHODJI DAJIBHAI DESAI.

In a recent paper (*J. Chem. Soc.*, 1932, 1079) the author has shown that when cyclopentane-*spiro*-cyclohexane-3:5-dione is methylated in presence of alcoholic sodium ethoxide a mixture of *c*-methyl-(I), *C*-dimethyl-(II), and *O*-methyl-(III) derivatives are formed.

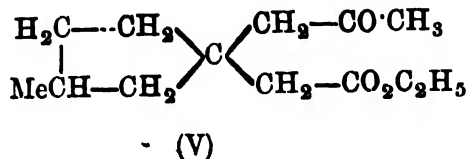


It appeared of interest to subject 3'-methylcyclopentane-*spiro*-cyclohexane-3:5-dione (IV) to this reaction in order to see how far the presence of a methyl group affected its course ; hence its synthesis was undertaken.

Two methods were tried. The condensation of 3-methylcyclopentenylacetone with ethyl sodiomalonate and hydrolysis of the resulting ester (*cf.* Vorländer, *Annalen*, 1897, 294, 258 ; also Norris and Thorpe, *J. Chem. Soc.*, 1921, 119, 1205). Though this condensation gave an excellent yield, the method proved unsatisfactory owing to the difficulties involved in the preparation of the requisite ketone in a good yield from 3-methylcyclopentenylacetic acid by Blaise-Maire reaction.

The second method was the ring-closure of the keto ester (V) which was prepared by the action of zinc methyliodide on the acid chloride of ethyl hydrogen 3-methylcyclopentane-1:1-diacetate.

Though the method involved a number of stages, the yield of the dione (IV) was so good that it could be recommended for its preparation.



The alkylation of this, as well as of some other diones, under a variety of conditions will form the subject matter of another communication.

#### EXPERIMENTAL.

##### *Dehydration of Ethyl 3-methylcyclopentane-1-ol-1-acetate.*

(i) *Phosphorus oxychloride method.*—A mixture of phosphorus oxychloride (12 c.c.), the hydroxy ester (16.8 g.) (Desai, *J. Chem. Soc.*, 1932, 1074), and benzene (30 c.c.) was heated on the water-bath until the evolution of hydrogen chloride ceased. The oil obtained by pouring the mixture into water was extracted with ether, washed with dilute sodium carbonate solution, dried, recovered and distilled when most of it boiled at 94.97°/10 mm. On redistillation *ethyl 3-methylcyclopentenyl acetate* boiled at 94.95°/10 mm. and had  $d_4^{21}$ , 0.9526;  $n_D^{21}$ , 1.4502, whence  $[R_L]_D$ , 47.4. (Calc., 47.87). (Found: C, 71.2; H, 9.7.  $\text{C}_{10}\text{H}_{16}\text{O}_2$  requires C, 71.4; H, 9.5 per cent).

(ii) *Thionyl chloride method.* (Darzens, *Compt. rend.*, 1911, 152, 1601).—Thionyl chloride (12 g.) was gradually added to an ice-cold solution of the hydroxy ester (16.6 g.) in pyridine (8 c.c.) and the mixture kept in ice for 2½ hours. The oil, precipitated on adding the mixture to dilute hydrochloric acid solution, was extracted with ether, washed alternately with dilute hydrochloric acid, sodium carbonate and water, dried, recovered and distilled when most of the liquid passed over at 96.99°/12 mm., leaving some undistillable residue. On redistillation the b.p. was 98.99°/12 mm., but the method was not found to be better than the phosphorus oxychloride method.

(iii) *Gaseous hydrogen chloride method.*—It was observed that partial dehydration of the hydroxy ester occurred when its alcoholic solution was saturated with gaseous HCl. But it did not offer any advantage over the first method.

**3-Methylcyclopentenylacetic acid.**—The unsaturated ester was hydrolysed with an excess of 10% aqueous alcoholic potassium hydroxide at room temperature and the acid isolated in the usual way. It boiled at 127-28°/12 mm., remained as a gum, and had  $d_4^{20}$ , 1.015;  $n_D^{20}$ , 1.4722, whence  $[R_L]_D$ , 38.54. (Calc., 38.01). (Found: C, 68.6; H, 8.7; Eq. wt., 139.0.  $C_8H_{12}O_2$  requires C, 68.6; H, 8.5 per cent. Eq. wt., 140). Attempts to prepare a solid dibromide were unsuccessful. The high molecular refraction is due to some  $\alpha\beta$ -isomer.

**3-Methylcyclopentenylacetone.**—3-Methylcyclopentenylacetic acid (14 g.) was heated with an excess of thionyl chloride for 1 hour and the acid chloride (b.p. 110-21°/21 mm.) was diluted with an equal volume of dry benzene. This was gradually added to a well-cooled solution of zinc methyl iodide [prepared by heating zinc-copper couple (16 g.), methyl iodide (8 c.c.), ethyl acetate (3 c.c.) and toluene (12 c.c.) for 12 hours] in toluene. The mixture was kept in ice for 4 hours and then decomposed with cold dilute sulphuric acid. The filtered toluene solution was extracted with ether, washed with water and ammonium sulphate, dried and distilled, when the ketone boiled at 93-94°/18 mm., yield 50%. (Found: C, 78.2; H, 10.3.  $C_9H_{14}O$  requires C, 78.3; H, 10.1 per cent). The *semi-carbazone* crystallised from dilute alcohol in needles, m.p. 185° (decomp.). (Found: C, 61.2; H, 8.7.  $C_{10}H_{17}ON_3$  requires C, 61.5; H, 8.7 per cent).

**Condensation of 3-methylcyclopentenylacetone with ethyl sodio-malonate: Synthesis of 3-methylcyclopentane-spiro-cyclohexane-8:6-dione (IV).**—The above ketone (13.8 g.) was gradually added to a well-cooled suspension of ethyl sodiomalonate in absolute alcohol (2.8 g. Na, 16 g. ethyl malonate and 30 c.c. alcohol), and the reaction was completed by heating for 12 hours on the water-bath. The resulting dione-ester was hydrolysed directly by adding caustic potash (25%, 50 c.c.) and heating for 6 hours. Alcohol was evaporated off and the aqueous solution was extracted with ether to remove the neutral impurities. The slightly acidic solution was heated on a sand-bath till the evolution of carbon dioxide ceased and the dione crystallised from the strongly acid solution on cooling. This was recrystallised from dilute alcohol in plates or from benzene-petrol mixture in cubes, m.p. 127-28°. The aqueous solution gave red colour with alcoholic ferric chloride solution.

(Found: C, 73.2; H, 9.0.  $C_{11}H_{16}O_2$  requires C, 73.8; H, 8.9 per cent).

The *methylene* derivative was immediately precipitated as an oil on adding formaldehyde to the saturated solution of the dione and solidified on standing and scratching. It crystallised from dilute alcohol in long slender needles, m.p. 161-62°. (Found: C, 74.0; H, 8.7.  $C_{23}H_{32}O_4$  requires C, 74.2; H, 8.6 per cent).

The *anilide*, prepared by heating the dione with an excess of aniline on a free flame for 15 minutes, solidified on rubbing with dilute hydrochloric acid. It crystallised from dilute alcohol (charcoal) in needles, m.p. 156°. (Found C, 80.1; H, 8.8.  $C_{17}H_{21}ON$  requires C, 80.0; H, 8.2 per cent).

*Synthesis of ethyl 3-methylcyclopentane-1-acetone-1-acetate.*—Ethyl hydrogen 3-methylcyclopentane-1: 1-diacetate (Desai, *J Chem. Soc.*, 1932, 1070) (23 g) was heated with thionyl chloride (20 c.c) for 2 hours and the excess of thionyl chloride removed. The crude acid chloride diluted with benzene (25 c.c.) was gradually added to a well-cooled toluene solution of zinc methyl iodide (1.2 mol.), and the mixture was decomposed with cold dilute sulphuric acid after 3 hours. The filtered toluene solution was extracted with ether, washed with water and ammonium sulphate solution, dried and distilled when most of it boiled at 152-55°/14 mm. (20 g.). This was hydrolysed with 50% caustic potash and the acid isolated in the usual manner. The keto-acid, which was admixed with the glutaric acid, was partially purified by extraction with light petrol (b.p. 40-60°), in which the keto-acid was freely soluble.

The *semicarbazone* of the acid crystallised from dilute alcohol in needles, m.p. 182° (decomp.) (Found: C, 56.4; H, 8.8.  $C_{13}H_{21}O_3N_3$  requires C, 56.5; H, 8.2 per cent).

*3-Methylcyclopentane-1-acetone-1-acetic acid*, regenerated from semicarbazone, boiled at 181-82°/12 mm. and remained as a viscous gum. It had  $d_4^{20}$ , 1.056;  $n_D^{20}$ , 1.4713, whence  $[R_L]_D$ , 52.41. (Calc., 52.58). (Found: C, 66.5; H, 9.8; Eq. wt., 198.5.  $C_{11}H_{16}O_3$  requires C, 66.6; H, 9.1 per cent. Eq. wt., 198).

The *ethyl ester*, prepared with alcoholic hydrogen chloride, boiled at 145°/14 mm. and had  $d_4^{21}$ , 0.9908;  $n_D^{21}$ , 1.4562, whence  $[R_L]_D$ , 62.0. (Calc., 61.7). (Found: C, 68.9; H, 9.8.  $C_{13}H_{20}O_2$  requires C, 69.0; H, 9.7 per cent).

The *semicarbasone* crystallised from dilute alcohol in leafy plates, m.p. 87-88°. (Found: C, 59.5, H, 8.9.  $C_{14}H_{23}O_3N_3$  requires C, 59.4; H, 8.8 per cent).

The ester (5 g.), dissolved in a solution of sodium (0.5 g.) in absolute alcohol (15 c.c.), was heated on the steam-bath for 6 hours, when it was quantitatively converted into 3'-methylcyclopentane-spiro-cyclohexane-3:5-dione (IV).

This work was carried out at the Imperial College of Science and Technology, South Kensington, London and I am grateful to Professor J. F. Thorpe, C.B.E., F.R.S., for his kind interest. My thanks are also due to the University of Bombay for a scholarship and to the Chemical Society for a grant that partly defrayed the cost.

DEPARTMENT OF CHEMISTRY,  
MUSLIM UNIVERSITY,  
ALIGARH.

Received May 11, 1933.



## **The Chemistry of Jute-lignin. Part II. Potash Fusion of Lignin.**

BY PULIN BEHARI SARKAR.

The structure of lignin still remains undetermined and the investigators appear to be divided mainly into three groups as to its nature. Klason (*Ber.*, 1920, **53**, 706, 1864), Heuser and Winsvold (*Cellulosechem.*, 1923, **4**, 49), Freudenberg (*Ber.*, 1929, **62**, 1554) from the chemical examination of lignin derivatives and its decomposition products hold that lignin contains the benzene nucleus together with oxidisable side chains; Herzog (*Ber.*, 1929, **62**, 1600) and Hägglund (*Svensk Kem. Tidskr.*, 1929, **41**, 185) from the study of ultraviolet absorption spectra of lignin derivatives conclude that lignin must contain at least one aromatic ring; while Strupp (*Cellulosechem.*, 1924, **5**, 6) and others consider lignin to be hydroaromatic in nature having for their support the results of pressure oxidation and vacuum distillation of lignin. The third group of workers, Willstätter and his collaborators (*Ber.*, 1922, **55**, 2637) maintain that lignin is entirely aliphatic in structure just like cellulose and pentosans with which it is closely related.

The problem has in recent years been complicated by the fact that lignins from different sources have been found to behave differently though the same methods have been applied for their study. Powell and Whittaker (*J. Chem. Soc.*, 1924, **125**, 357) who made a thorough examination of flaxwood-lignin, observed on comparing their results with those of Cross and Bevan for jute-lignin, "Thus, jute-lignin is essentially different from flax-lignin." It appears rather unlikely that lignins from different woods have different compositions. The anomalous behaviour of lignins from different sources would just as well be explained by the degree of polymerisation. Before any definite formula can be assigned to lignin it is necessary to establish the identity of structure of the different lignins. Hence the importance of studying the decomposition products of lignins from all possible sources.

Jute-lignin was first studied as lignone chloride by Cross and Bevan (*J. Chem. Soc.*, 1882, 41, 90) who assigned the formula  $C_{19}H_{22}O_8$  to the "aromatic constituent" of jute-fibre. They also observed the great resemblance between jute-lignin (which they did not isolate) and catechin though they could not separate any product therefrom similar to the latter. Subsequently (*Ber.*, 1893, 26, 2620) they were struck by the yellow colour of the chloro compound of lignin similar to that of quinones from which they suggested a ketonic structure.

The large volume of experimental data obtained from the study of lignins from different woods cannot be explained by the ketonic formula unless we assume jute lignin to be essentially different from others. Since then no work has been done on jute-lignin; the above-mentioned authors worked with lignocellulose and not with isolated lignin, and their results are difficult to interpret. Hence it was thought worth while to make a systematic study of lignin isolated from jute in order to see if it really differed from others. In an earlier paper (*J. Indian Chem. Soc.*, 1931, 8, 397) it was shown by the author that lignin extracted from jute-fibre had generally speaking almost similar properties, both physical and chemical, to some wood-lignins. In the present investigation, alkali fusion under different conditions has been studied with a view to see if it gave identical decomposition products. The results obtained confirm the view that jute-lignin is in many respects similar to, if not identical with, other lignins.

Willstätter's method has been found by the author (*loc. cit.*) to be the best for the isolation of lignin from jute, used in this investigation. The potash fusion was carried out at different temperatures, for varying times, under different atmospheres and in different vessels. Temperature has been found to be the most important factor and time the next. At temperatures above  $240^{\circ}$  only traces of protocathechuic acid and pyrocatechol could be obtained; above  $260^{\circ}$  none, whilst if the fusion was continued for more than one hour, the yield of these bodies rapidly diminished, even if the temperature was kept below  $240^{\circ}$ . Iron was shown by Heuser (*loc. cit.*) to have a catalytic effect on the potash fusion causing a higher yield of aromatic substances, while by using zinc dust Rassow and Zickmann (*J. pr. Chem.*, 1929, ii, 123, 189) was able to increase the yield of protocathechuic acid from 8 to 15%. No such improvement could be observed in the case of jute-lignin, when fused in an iron crucible in



the presence of zinc dust at temperatures specified by the authors. Obviously jute-lignin is more susceptible to the action of fused alkali than wood-lignins and is acted upon at lower temperatures. The poor yield of aromatic substances at relatively high temperatures and for prolonged times is explained by the fact that both protocatechuic acid and pyrocatechol are more or less rapidly decomposed to carbon dioxide and oxalic acid, by the oxidising action of the fused potash (Heuser and Winsvold, *loc. cit.*). The best yield of aromatic bodies was obtained by fusing jute-lignin at 220-30° for 1 hour, all the lignin being added as quickly as possible at 200°. More oxalic acid was obtained at higher temperatures but less lignic acid. No lignic acid was found at 300° when the fusion was continued for 3½ hours, oxalic acid being the only product. With wood-lignin this is not the case. With iron vessel and in an atmosphere of nitrogen only a slightly higher yield of aromatic bodies could be obtained, the maximum being 13.87%. In an atmosphere of carbon dioxide more oxalic acid was obtained but with no improvement in the yield of aromatic substances.

Butyric acid has been identified as a product of fusion of jute-lignin, the highest yield was 9.13%. No trace of vanillic acid could be detected in any of the numerous fusions carried out with jute-lignin nor any product containing any methoxy group. The formation of butyric acid indicates the presence of a side chain of at least 4 carbon atoms in the lignin molecule. Cross and Bevan's formula contains a chain but with two CO groups which cannot explain the formation of butyric acid. Again, the aromatic ring with two CO groups in 1:5 positions cannot give catechol. Lastly, protocatechuic acid has the OH groups in 3:4 positions with respect to the COOH group. In the lignin molecule the carboxyl group must have been formed by the oxidation of a side chain and the OH groups were either already present or have been formed from OCH<sub>3</sub> group in those positions. These do not occur in Cross and Bevan's formula, which is therefore untenable.

Hawley and Harris (*Ind. Eng. Chem.*, 1932, **24**, 873) are recently reported to have prepared lignin by heating purified wood or cellulose in sealed tubes at 188° for a maximum period of 8 days. It was similar to lignin as regards resistance to hydrolysis, chlorination, sulphide reaction, ultraviolet absorption spectrum and reducing value. They called it synthetic lignin. Jute after complete delignification by chlorine peroxide was subjected to

the same treatment, exactly under the same conditions. The white fibre turned brown and brittle. Lignin was isolated therefrom by Willstätter's method, but the brown fibre did not respond to the colour tests with aniline acetate and phloroglucinol, usually given by ordinary jute. However, the black mass, obtained after hydrolysis of the cellulose, possessed physical resemblance to genuine lignin. On fusion with potash at  $220-30^{\circ}$  in the usual way, no carbon dioxide or any other gas was evolved and no smell was perceptible. It was only partly dissolved by the alkali. On adding water, a light brown powder separated. The pale brown solution was examined for protocatechuic acid and other similar acids but none could be detected, not even oxalic acid. Thus, the so-called synthetic lignin is chemically different from genuine lignin.

Raw jute was delignified by moist chlorine peroxide gas, complete removal of lignin was ascertained by dissolving the milk-white fibre in 72%  $\text{H}_2\text{SO}_4$  to a colourless solution. The fibre was then fused at  $220-30^{\circ}$  with caustic potash exactly in the same way as in the case of lignin. The fused mass was pale yellow and the aqueous solution gave no precipitate with dilute sulphuric acid. On steam distillation only formic and acetic acids were identified but no butyric acid. The alcoholic extract gave oxalic acid in large amounts and nothing was obtained by extraction with ether. Hence, aromatic substances are constituent parts of the lignin molecule, which must, therefore, be aromatic in nature. It is much more likely that the drastic oxidising action of fused alkali causes the decomposition of a complex molecule to simple ones, rather than the formation of aromatic bodies from aliphatic ones.

#### EXPERIMENTAL.

Caustic potash (25 g.), dissolved in water (10 c.c.), was heated to  $200^{\circ}$  in a large nickel crucible, provided with a nickel tube, sealed at one end or better an iron tube containing a little mercury to protect the thermometer and finely powdered lignin (5 g.) was rapidly added to the molten mass with vigorous stirring. (The lignin should be added at a temperature lower than that of fusion since the reaction is exothermic.) The mass frothed up and a pink colour developed. In order to keep the mass in the liquid state caustic potash (25 g. in 10 c.c. water) was again added after half an hour. A characteristic smell was given off during the fusion,

It is difficult to detect the end point but by repeated trials one hour has been found to be the optimum duration. At higher temperatures the mass became deep brown and finally black in which case no protocatechuic acid could be detected. At  $300^{\circ}$  for  $8\frac{1}{2}$  hours a white mass was obtained giving only oxalic acid.

The mass was cooled, dissolved in the minimum quantity of water and acidified with 30%  $\text{H}_2\text{SO}_4$ . After 2-3 hours the lignic acid separated and a clear light brown liquid was obtained by filtration. The lignic acid was washed with lukewarm water until free from  $\text{H}_2\text{SO}_4$ , dried at  $105^{\circ}$  and weighed.

The filtrate with the washings was subjected to steam distillation, until the distillate was neutral. Butyric acid was detected in the distillate, but no phenol.

The liquid left in the distilling flask was neutralised with  $\text{Na}_2\text{CO}_3$  and evaporated to dryness on the water-bath. The acidified dry residue was extracted with absolute alcohol in a soxhlet apparatus. After the removal of alcohol, the residue was exhaustively extracted with dry ether. The undissolved solid was treated with water, made alkaline with ammonia and oxalic acid precipitated by a boiling solution of  $\text{CaCl}_2$ . This was washed, dried in the steam oven and weighed.

The residue from the ether extraction was then treated with benzene in the cold. Pyrocatechol was obtained in solution while protocatechuic acid remained undissolved. The quantitative figures refer to a fusion done at  $220-30^{\circ}$  in air in which 5.25 g. of lignin were taken. Results of other experiments are given in a tabular form in the next page.

*Lignic acid.*—1.291 G. was obtained from 5.25 g. (24.6 % of the lignin taken). It is a black amorphous solid which reduces Fehling's solution, contains no methoxy group (Zeisel), does not react with  $\text{Cl}_2$  in aqueous suspension. It dissolves readily in alcohol but is not precipitated by ether. It contains no potassium, has 0.87% ash. A part of it was fused again at  $240-60^{\circ}$  with potash in the usual way for  $2\frac{1}{2}$  hours. The whole of it did not react with  $\text{KOH}$  and oxalic acid was the only product. The other part was then fused at  $220-80^{\circ}$  for  $1\frac{1}{2}$  hours. Protocatechuic acid and oxalic acid were detected in the fused mass. Thus lignic acid appears to be the precursor of protocatechuic acid and hence of catechol.

*Butyric acid.*—The distillate from the steam distillation was made alkaline with  $\text{Na}_2\text{CO}_3$ , evaporated to dryness on the water-bath

Temp.	Time.	Lignic acid.	Butyric acid.	Oxalic acid (anhydrous).	Protocatechuic acid.	Pyrocatechol.	Remarks.
280-300°	3½ hr.	Nil	Nil	20·7%	Nil	Nil	Ni, crucible in air.
240-285°	1½	18·2%	...	...	Nil	Nil	Fe crucible, in air with zinc dust.
240-280°	1½	20·3	8·3%	...	traces	Nil	Ni vessel, in air with zinc dust.
220-230°	1	24·6	9·13	18·72	12·1%	3·5%	Ni vessel, in air.
" "	"	"	...	17·6	13·87	3·64	Fe vessel, in N <sub>2</sub> .
220-250°	"	22·0	8·7	19·2	4·7	...	Ni vessel, in air.
" "	"	...	...	20·86	4·85	...	Fe vessel, in C <sup>12</sup> .
180-200°	2	33·3	...	15·7	traces	Nil	Ni vessel, in air.
220-230°	"	23·5	...	...	9·6	2·7	Do

and the residue acidified with strong  $\text{H}_2\text{SO}_4$ . The characteristic smell of butyric acid was at once perceptible. The mixture was then warmed cautiously with a little alcohol and the sweet pineapple odour of the butyric ester confirmed the acid. The solution of Ca-salt appeared as a precipitate on boiling. As no other acid could be detected, the acid-distillate from the fusion product in question was titrated with  $N/10\text{-NaOH}$  with phenolphthalein as indicator ; 53.9 c.c. of it was required, so 9.13% of butyric acid was obtained.

*Oxalic acid.*—The aqueous solution of the ether-insoluble residue gave a white precipitate with  $\text{CaCl}_2$  insoluble in acetic acid and ammonia but soluble in mineral acids. It readily decolourises warm acidified  $\text{KMnO}_4$ . The acidified solution was concentrated and kept in the vacuum desiccator, crystals of oxalic acid appeared which melted at  $101^\circ$ . [Found:  $\text{CaO}$ , 38.29.  $\text{Ca}(\text{COO})_2\text{H}_2\text{O}$  requires  $\text{CaO}$ , 38.35 per cent]. The Ca-salt was dissolved in dilute  $\text{H}_2\text{SO}_4$  and the acid estimated volumetrically with  $N/10\text{-KMnO}_4$ . 10 C. c. of the solution (made 500 c.c. from 5.25 g. lignin) required 4.35 c.c. of  $\text{KMnO}_4$ , which corresponds to 18.72% of anhydrous oxalic acid.

*Protocatechuic acid.*—The residue of the ether extraction was separated by cold benzene into two fractions. The insoluble part was a light brown powder which could not be decolorised in aqueous solution with animal charcoal. It gives bluish green colour with  $\text{FeCl}_3$ , which turns deep red with a drop of sodium carbonate solution. It turns Fehling's solution green at once and reduces slowly and it also reduces ammoniacal silver nitrate in the cold. It decolourises acid potassium permanganate rapidly and gives with lead acetate a white lead salt soluble in acetic acid. A slightly acid solution of lead acetate also precipitated the salt which was washed and dried. The finely powdered salt was suspended in ether and sulphuretted hydrogen passed into it. The ethereal solution of the acid was crystallised from water, m.p.  $196^\circ$  (mixed m. p. with Merck's pure sample showed no depression). From 5.25 g. of lignin the residue after extraction with benzene amounted to 0.6350 g. (12.1%).

*Catechol.*—The pale grey residue after evaporation of benzene was decolourised and crystallised from benzene in rectangular blocks. Dried over sulphuric acid in vacuum it melted sharply at  $103^\circ$ . A mixed melting point with Kahlbaum's product was exactly the same. It was very easily soluble in water and it reduces neutral silver nitrate readily in the cold. It gives a green coloration with ferric

chloride and turns red with sodium carbonate solution. The aqueous solution with alkalis remains colourless. Neutral lead acetate precipitates the white lead salt which is readily soluble in acetic acid. Neutral potassium permanganate is decolourised in the cold. From 5.25 g. of lignin 0.1840 g. of catechol was obtained (3.5%).

#### SUMMARY.

(1) By the potash fusion of jute-lignin oxalic, butyric and protocatechuic acids, and pyrocatechol besides lignic acid have been obtained.

(2) The formation of these products proves conclusively that jute-lignin is not essentially different from various other wood-lignins.

(3) Delignified jute-fibre gave neither aromatic substances nor butyric acid when similarly treated.

(4) Cross and Bevan's formula has been shown to be untenable as it cannot explain the formation of these products.

(5) Jute-lignin has been found to be attacked at a comparatively lower temperature than wood-lignins and the best yield has been obtained at 220-30° for one hour,

(6) Lignic acid is the precursor of protocatechuic acid and so of catechol.

(7) The so-called synthetic lignin has been shown to be different from native lignin in jute.

I take this opportunity of expressing my grateful thanks to Principal D. N. Sen, M.A., and Prof. B. K. Chowdhury, M.Sc. for giving me facility for work. My best thanks are also due to Prof. J. C. Ghosh, D.Sc. and Dr. J. K. Chowdhury, Ph.D. for encouragement and valuable suggestions.

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## 6-Aldehydo-4-methyl- $\alpha$ -naphthapyrone and Dyes Derived from it.

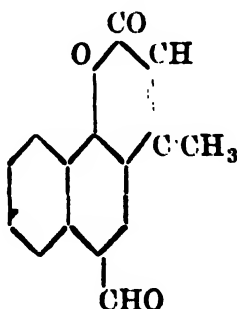
By RAJENDRA NATH SEN AND GOPAL CHANDRA MUKHERJEE.

6-Aldehydocoumarin was previously obtained by the application of Reimer and Tiemann's reaction on coumarin (Sen and Chakravarti, *J. Amer. Chem. Soc.*, 1928, **50**, 2428). 4-Methyl- $\alpha$ -naphthapyrone similarly yields about 30% of an aldehyde, the aldehydic group entering the 6-position (*para* to original OH group) there being no other possibility. The aldehyde does not melt up to 300°, it readily gives a phenylhydrazone (m. p. 125°), a semicarbazone (m.p. 260°) and an oxime (which does not melt up to 260°).

The aldehyde condenses with dimethylaniline to produce a leuco base of a triphenylmethane dye which on oxidation gives the carbinol, the salt of which produces a bluish-green shade on silk and wool. A pyronine dye has been obtained by condensing the aldehyde with four molecules of resorcinol, when the C=O group in the lactone ring as well as the aldehyde group react. Silk is dyed a bright orange shade by the sodium salt of this compound.

### EXPERIMENTAL.

#### 6-Aldehydo-4-methyl- $\alpha$ -naphthapyrone.



A solution of 4-methyl- $\alpha$ -naphthapyrone (10.5 g.) (obtained by the condensation of  $\alpha$ -naphthol and acetoacetic ester in presence of sulphuric acid, Bartsch, *Ber.*, 1903, **36**, 1966) in caustic soda (14 g.

in 40 c.c. of water) was heated on the water-bath for 10-12 hours with gradual addition of a mixture of chloroform (10 c.c.) and alcohol (30 c.c.). The temperature was kept initially at 80° for the first 3 hours, the solution being mechanically stirred throughout. The deep red solution turned first deep blue on the addition of chloroform and alcohol and changed to red again after 6-7 hours. The solution, after removing alcohol and chloroform on a water-bath was acidified with acetic acid when a pasty gelatinous solid separated out. This was collected, dried, and washed several times with chloroform to remove any excess of the mother substance. The residue was dried and crystallised from glacial acetic acid (charcoal) as brown microcrystalline needles, m.p. above 280°, yield 3.5 g.

It is insoluble in water, chloroform, benzene and ether; moderately soluble in alcohol and acetone and very readily soluble in hot glacial acetic acid. (Found: C, 74.78; H, 4.31.  $C_{15}H_{10}O_3$  requires C, 75.63; H, 4.2 per cent).

The *phenylhydrazone*, prepared in the usual manner, crystallised as yellow needles from dilute acetic acid, m. p. 125°. (Found: N, 9.25.  $C_{21}H_{16}O_2N_2$  requires N, 8.53 per cent).

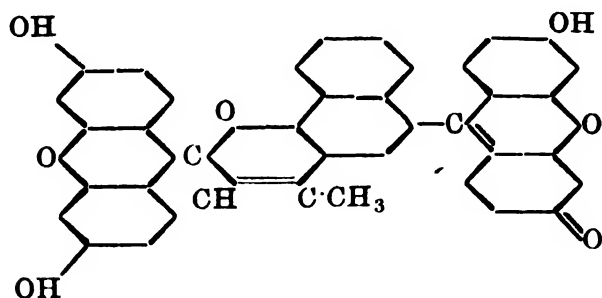
The *semicarbazone*, prepared in the usual manner, separated as chocolate brown needles from dilute alcohol, m. p. 260°. (Found: N, 15.31,  $C_{16}H_{13}O_3N_3$  requires N, 14.23 per cent).

*Oxime*.—The aldehyde (2 g.) was dissolved in the smallest amount of dilute caustic soda solution and to this solution was added a saturated solution of hydroxylamine hydrochloride (5 g.) and the solution heated on a boiling water-bath with an air condenser for 4.5 hours. It was then cooled and acidified with dilute hydrochloric acid and the precipitate dried. It crystallised from alcohol as red microcrystalline needles not melting below 280°. (Found: N, 5.54.  $C_{13}H_{11}O_3N$  requires N, 5.53 per cent).

*Condensation of the aldehyde with dimethylaniline*.—The aldehyde (2 g.) was dissolved in dimethylaniline (10 c.c.) and the solution heated on a boiling water-bath for 30 hours with frequent additions of concentrated hydrochloric acid (10 c.c. in all). It was isolated as usual and finally crystallised from alcohol as greenish-white powder not melting below 250°. It is moderately soluble in alcohol and acetone and soluble in both acid and alkali. (Found: N, 6.5.  $C_{31}H_{30}O_2N_2$  requires N, 6.06 per cent).

When the leuco base, thus obtained, is oxidised with lead peroxide, it dyes silk a beautiful greenish-blue shade.



*Condensation of the Aldehyde with Resorcinol.*

A mixture of the dry aldehyde (1 mol., 1.5 g.), dry resorcinol (4 mol., 5 g.) and concentrated sulphuric acid ( $d$  1.84, 2 c.c.) was heated first, in a boiling water-bath for 2-3 hours and then on an oil-bath at 120-130° for 5-6 hours with an air condenser. It was then isolated in the manner described by Sen and Chakravarti (*loc. cit.*).

The formula is based on the fact that the analogous condensation product of 6-aldehyde-coumarin with resorcinol possesses a similar formula giving a tripotassium salt (Sen and Chakravarti, *loc. cit.*). It does not melt below 280° and is soluble in alcohol and acetone, insoluble in ether and benzene. Silk is dyed a bright orange shade by its sodium salt. (Found: C, 77.16; H, 4.03.  $C_{39}H_{24}O_7$  requires C, 77.49; H, 3.97 per cent).

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## Complex Compounds of Iridium. Part II. Compounds of Organic Sulphides and Pyridine.

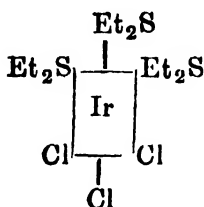
BY PRAFULLA CHANDRA RAY, NADIABEHARI ADHIKARI AND  
RANAJIT GHOSH.

In a previous communication (*J. Indian Chem. Soc.*, 1932, 9, 251) it has been stated that during reaction with organic sulphides, iridium tetrachloride first loses chlorine and that this reaction becomes accelerated in presence of alcohol. We have since then tried the same reaction in other media, *e.g.*, acetone, chloroform and benzene. In acetone, the reaction yields the same compound  $\text{IrCl}_3 \cdot 3\text{Et}_2\text{S}$  even in cold along with a tarry residue. No appreciable reaction, however, takes place in chloroform but a very feeble reaction is noticed in presence of moisture, though no sufficient quantity for analysis could be separated. In benzene, even when heated with constant shaking for 6-8 hours, there is no reaction and like platonic chloride, iridium chloride reacts with ethyl sulphide, methyl sulphide, diethyl disulphide or dimethyl disulphide in absence of alcohol or acetone, etc., though after prolonged contact, with evolution of hydrochloric acid. Moreover, even in presence of dilute aqua regia, in alcohol the same product  $\text{IrCl}_3 \cdot 3\text{Et}_2\text{S}$  is obtained. All these point to the fact that iridium chloride in solution is first reduced and then reacts with the sulphide present; the presence of a small amount of chlorine in solution cannot prevent the reduction. That iridium trichloride is formed, has been further proved by the isolation of its soluble variety when dimethyl disulphide was allowed to act on iridium tetrachloride in alcohol in presence of a small amount of aqua regia (this will form the subject of a subsequent communication).

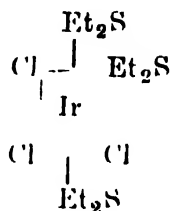
It has already been shown (*loc. cit.*) that by the action of ethyl sulphide on iridium tetrachloride in presence of hot alcohol under reflux, a compound of the formula  $\text{IrCl}_3 \cdot 3\text{Et}_2\text{S}$  (m. p.  $181^\circ$ ) was obtained. It was noticed there that a very minute quantity of an insoluble powder also separated. The yield of this substance has

been found to increase if the above reaction is conducted in cold. It possesses the same chemical composition as the other compound but differs from it in colour, solubility and melting point. The present compound, when crystallised from hot acetone, is obtained in brownish-red shining needles but when powdered or precipitated from its solution, it is of light pink colour and is stable even when heated up to 200°. It is insoluble in benzene, sparingly so in alcohol and acetone but extremely soluble in chloroform, whereas the previous orange coloured substance is extremely soluble in benzene and also soluble in most of the organic solvents including ether.

Theoretically two isomers of  $\text{IrCl}_3 \cdot 3 \text{Et}_2\text{S}$  are possible, *e.g.*,



Cis (I)



Trans (II)

By his exhaustive works on isomerism in iridium complexes, Delepine has established that the *cis*- compound is always orange and the *trans*, red. By analogy, the constitution of the red compound should be (II) and that of the orange one, (I). By the action of pyridine on (I), two compounds of the formulae  $\text{IrCl}_3 \cdot \text{Py} \cdot 2\text{Et}_2\text{S}$  and  $\text{IrCl}_3 \cdot 2\text{Py} \cdot \text{Et}_2\text{S}$  have been obtained. Both the compounds are orange-yellow, soluble in acetone and extremely so in chloroform and pyridine and have sharp melting points. Their acetone solutions do not give any precipitate with silver nitrate in the same solvent. The remaining  $\text{Et}_2\text{S}$  could not be replaced by pyridine even when the reactants were heated in a sealed tube at 140-50° for 10 hours. These may be represented as :



(III)



(IV)

The melting point rises gradually as each of the  $\text{Et}_2\text{S}$  group is replaced by pyridine, *e.g.*, (I) melts at 181°, (III) at 171-72°, and

(IV) at 260°. Similar cases of partial replacement of ethyl sulphide by pyridine, ethylamine and piperidine, etc., is not uncommon in platinum compounds (*cf. J. Indian Chem. Soc.*, 1926, 3, 361).

By the action of benzyl sulphide on iridium tetrachloride  $\text{IrCl}_3 \cdot 3\text{Bz}_2\text{S}$  has been obtained. As the chlorine does not ionise in solution, it can be represented like (I). Along with this, a red compound is also formed but it has not yet been isolated in the pure state.

#### EXPERIMENTAL.

*Preparation of  $\text{IrCl}_3 \cdot 3\text{Et}_2\text{S}$  (red variety, m.p. 171°).*—Iridium tetrachloride (8 g.) and ethyl sulphide (8 c.c.) in alcohol (30 c.c.) were mixed together and kept corked for 12 days with occasional stirring and then the solution filtered to separate a very small quantity of greyish black mass, probably reduced iridium, which gradually formed during the reaction. The deep red filtrate was then concentrated in vacuum over calcium chloride for 2 days when a crystalline substance separated out. The crystals were collected, washed free from the adhering liquid with benzene and finally with cold acetone, m.p. 159-60°. This on further crystallisation (4 times) from a mixture of chloroform and acetone melts at 171°. It is a brownish-red shining substance but when obtained as a precipitate from chloroform or acetone solution or powdered, it is flesh coloured. The filtrate was then treated as recorded in the previous paper (*loc. cit.*). (Found: Cl, 17.92; S, 16.9, 17.3; Ir, 33.6.  $\text{IrCl}_3 \cdot 3\text{Et}_2\text{S}$  requires Cl, 18.68; S, 17.08; Ir, 33.86 per cent).

*Preparation of  $\text{IrCl}_3 \cdot \text{Py} \cdot 2\text{Et}_2\text{S}$ .*—To a solution of  $\text{IrCl}_3 \cdot 3\text{Et}_2\text{S}$  (2 g.) in benzene (20 c.c.), pyridine (3 c.c.) was added and the mixture heated under reflux on a water-bath for 10-12 hours and then for another 6-7 hours without a condenser. Shining yellow crystals separated out on cooling. These were collected, washed with a small quantity of cold benzene and digested with acetone (hot) when almost the whole of the substance went into solution leaving a very small quantity, also insoluble in hot chloroform and pyridine, melting at 222° (decomp.). From the acetone solution, glistening yellow crystalline substance was obtained and this when twice crystallised from the same solvent melted at 171-72°. The main filtrate on dilution with a mixture of acetone and water yielded the above substance, m. p. 171-72°, when crystallised

several times from acetone. It is soluble in benzene and acetone sparingly so in alcohol but freely in chloroform. In acetone solution it does not give any precipitate with silver nitrate in the same solvent. (Found: Cl, 19.2; S, 11.0; Ir, 34.25.  $\text{IrCl}_3 \cdot \text{Py} \cdot 2\text{Et}_2\text{S}$  requires Cl, 19.05; S, 11.4; Ir, 34.5 per cent).

*Preparation of  $\text{IrCl}_3 \cdot \text{Et}_2\text{S} \cdot 2\text{Py}$ .*— $\text{IrCl}_3 \cdot 8\text{Et}_2\text{S}$  (1.5 g.) in pyridine (5 c. c.) was heated in a sealed tube for 4 hours at 120–25° and then for another 4 hours at 145–50°. Before heating, the  $\text{IrCl}_3 \cdot 8\text{Et}_2\text{S}$  was in solution but after heating and cooling the tube a fair amount of a yellow crystalline substance was found to separate (B). The pyridine solution was decanted off and this on dilution yielded a dirty yellow precipitate. It was collected and crystallised from acetone, m. p. 286–40°(A); but on fractionally crystallising it thrice from acetone, the melting point rose up to 258° and on analysis found to be identical with (B). The solid crystalline substance was washed with acetone (cold) and ether to remove the last trace of pyridine and then crystallised from hot chloroform, m. p. 258°. When again dissolved in acetone, it was found that a very small portion containing a white and a red substance did not pass into solution but the quantity being too small it was not further dealt with. The melting point was finally found to be 260° (B). (Found: N, 4.8; S, 5.76; Cl, 19.7; Ir, 35.37.  $\text{IrCl}_3 \cdot \text{Et}_2\text{S} \cdot 2\text{Py}$  requires N, 5.1; S, 5.85; Cl, 19.4; Ir, 35.28 per cent).

*Preparation of  $\text{IrCl}_3 \cdot 3\text{Bz}_2\text{S}$ .*—In a stoppered conical flask, iridium chloride (6 g.), benzyl sulphide (18.6 g.) and alcohol (75 c. c.) were taken together and kept closed. The chloride took about 4 hours to go into solution and the sulphide about 20 hours. After 24 hours a yellow precipitate began to separate slowly and this, once begun, went on for a week when a tarry substance was first noticed to separate along with the yellow substance. The solid substance was then collected and dissolved in benzene from which on spontaneous evaporation, it was obtained in pale yellow colour, m. p. 201°. It is highly soluble in benzene and chloroform. (Found: Cl, 11.2; S, 9.76; Ir, 20.4.  $\text{IrCl}_3 \cdot 3\text{Bz}_2\text{S}$  requires Cl, 11.81; S, 10.19; Ir, 20.49 per cent).

*Action of ethyl sulphide on ammonium chloriridate.*—Ethyl sulphide (2 c. c.) was added to ammonium chloriridate (about 2 g.) in water (50 c. c.) and alcohol (6 c. c.) and it was heated under reflux on a water-bath for 8–10 hours, when gradually a yellow substance separated out, mixed with a little of a red variety. The solid substance

was separated and digested under reflux with acetone. This extract on concentration yielded  $\text{IrCl}_3 \cdot 3 \text{Et}_2\text{S}$  mixed with a small quantity of a dirty white substance having no m. p. The insoluble residue (m. p.  $210^\circ$ ) was then crystallised twice from chloroform in which it was found to be slightly soluble, m. p.  $222^\circ$  (decomp.). In our previous paper (*loc. cit.*) the m. p. of this compound was stated to be  $207^\circ$  at which it decomposes. But now on recrystallising the same sample 4 times from chloroform, it has been found to melt with decomposition at  $222^\circ$ . (Found: S, 13.53; Ir, 41.74.  $\text{Ir}_2 \text{Cl}_3 \cdot 4 \text{Et}_2\text{S}$  requires S, 13.86; Ir, 41.82 per cent).

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## Preparation and Properties of Zirconium Sulphosalicylic Acid Jellies.

BY SATYA PRAKASH.

Berkmann and Zocher (*Kolloid Z.*, 1927, **42**, 309, 322), Wo. Ostwald and Mortens (*Koll.-chem Beih.*, 1926, **23**, 242) and others have made detailed investigations of the properties of mercury derivatives of sulphosalicylic acid which are known to form colloidal suspensions in water and which exhibit marked anisotropy, and double refraction. The author (*J. Indian Chem. Soc.*, 1930, **7**, 367) has also studied the conditions of formation of the jellies of mercuri-sulphosalicylic acid. Recently, the author has succeeded in preparing the jellies of zirconium sulphosalicylic acid for the first time and in the present communication, an account will be given of the conditions of the formation of this jelly.

Even in dilute solutions, zirconium oxychloride forms a stable solution and it does not develop any opalescence when kept for a long time. However, if its dilute solution be boiled and allowed to dialyse, it hydrolyses and gives a transparent sol of zirconium hydroxide. When a concentrated solution of zirconium oxychloride is mixed with a concentrated solution of sulphosalicylic acid, it forms a colourless mixture. Now, if to this transparent mixture be added water to a certain dilution, opalescence at once develops, and finally, the whole of the solution becomes completely opaque. After some time, a precipitate also appears, which settles down, leaving a clear supernatant liquid. The author has found that by careful regulation of the concentrations of zirconium oxychloride, sulphosalicylic acid and water, not only stable colloidal sol of zirconium sulphosalicylic acid is obtained, but very transparent glass-like hard jellies can also be prepared.

In the following experiments, a 50 % solution of 5-sulphosalicylic acid,  $C_6H_3SO_3H \cdot OH \cdot COOH$ ,  $2H_2O$ , (8.99N), was used which was free from sulphate ions. An almost saturated solution of zirconium oxychloride,  $ZrOCl_2$ , corresponding to 810.68 g.  $ZrO_2$  per litre was found to be very suitable for jelly formation. The time of

setting and the nature of the jellies obtained at different concentrations are given in the following tables. The jelly forming components were thoroughly mixed in test tubes which were allowed to stand for a number of days.

TABLE I.

Amount of zirconium oxychloride soln. used each time = 1 c.c.

Amount of sul- phosalicylic acid.	Amount of water.	Time of setting and the nature of the jelly.
0.5 c.c.	0 c.c.	Clear solution, no jelly even in 4 days
0.5	0.5	do do do
0.5	1.0	do do do
0.5	1.5	Transparent jelly in 85 hrs.
0.5	2.0	Transparent jelly in 72 hrs.
0.5	2.5	Transparent jelly in 50 hrs
1.5	0	Slight precipitate but no jelly
1.5	0.5	No jelly within 4 days
1.5	1.0	Transparent jelly within 60 hrs
1.5	1.5	Transparent jelly with slight opalescence in 40 hrs.
1.5	2.0	Opalescent jelly in 30 hrs.
2.0	0	Transparent jelly in 78 hrs
2.0	0.5	Transparent jelly in 46 hrs.
2.0	1.0	Transparent jelly in 46 hrs.
2.0	1.5	Opalescent jelly in 40 hrs.
2.0	2.0	Translucent jelly in 10 hrs.
2.0	3.0	Translucent jelly in 10 hrs.

From the results recorded in the above table, it would be seen that (i) the greater the amount of water added to a particular mixture of zirconium oxychloride and sulphosalicylic acid, the less is the setting time of the jelly, but the jelly is more opalescent, (ii) the jellies obtained with the same amount of zirconium oxychloride and water but with varying concentrations of sulphosalicylic acid show that an increase in the concentration of sulphosalicylic acid causes also a decrease in the time of setting. It is a general rule, that where a jelly has a marked tendency of developing opalescence, the time of the setting of the jelly is less and the speed of development of turbidity is more rapid. Even the jellies which have only a slight opalescence at the time of setting become almost opaque if kept for a large number of days.

In a previous publication (*J. Indian Chem. Soc.*, 1932, 9, 193) the author has studied the influence of temperature on the setting of numerous iporganic jellies and also mercuri-sulphosalicylic acid jelly. The influence of temperature is also very much marked in the case of zirconium sulphosalicylic acid jelly. In the following table, the results are recorded concerning the setting of a jelly prepared by the addition of 1 c. c. of zirconium oxychloride solution to 2 c. c of sulphosalicylic acid and 2 c. c. of water. The contents were allowed to set in baths maintained at different temperatures.

TABLE II.

Temperature	Time of setting	Nature of the jelly
80°	1 min	Opaque
70°	2	Opaque with slight light transmission
60°	11	Translucent at the time of setting but becoming opaque just after a few minutes
55°	22	Translucent jelly
50°	35	Translucent jelly
45°	75	Translucent jelly
40°	240	Transparent with slight opalescence
30°	19 hrs.	Transparent with very slight opalescence

Thus zirconium sulphosalicylic acid jelly is more readily obtained at a higher temperature, but the texture and fineness of the jelly are markedly spoiled.

Some of the best jellies of zirconium sulphosalicylic acid are as transparent as mercuri-sulphosalicylic acid jellies, but on ageing they become comparatively harder than the mercuri- ones. These zirconium jellies do not undergo any syneresis, but on drying exhibit a peculiar sort of rupture with beautiful pattern of cracks. This is due to the high concentration of the jelly which yields a hard compactness. Mercuri- jellies are obtained at comparatively low concentrations. If the jelly producing solutions of zirconium jelly are allowed to set at a high temperature, an opaque mass is obtained; but if a transparent jelly set at ordinary temperature and kept for a sufficient number of days be now transferred to a bath maintained at a high temperature, the opalescence is not so rapidly

developed. In this respect the jelly is quite resisting to the temperature.

The influence of some ions on the setting of the jelly has also been investigated. The following table shows the influence of potassium chloride and ammonium sulphate.

TABLE III.

Zirconium oxychloride solution used=1 c. c. Sulphosalicylic acid added=2 c. c. Total volume kept=5 c. c. by adding water.

N-KCl in c. c.	0	0.5	1.0	1.5	
Time of setting in hrs.	19	26	27	29	
N/5-Ammonium sulphate in c.c.	0	0.3	0.7	1.1	1.5
Time of setting in hrs.	19	11	10.25		Precipitate appearing in $\frac{1}{2}$ hr. but setting to a solid mass in $6\frac{1}{2}$ hrs.

Thus it would be seen, that in presence of monovalent ions, like chlorine from potassium chloride, the sol of zirconium sulphosalicylic acid is markedly stabilised. Similar stabilisation is observed in the case of aluminium nitrate. In the presence of ammonium sulphate or any sulphate, the coagulation is rapid and a jelly is obtained in a comparatively less time. The jellies obtained in the presence of sulphate ions are more opaque too. The sensitising influence of citrate ions is all the more marked and in presence of even very small concentrations of sodium citrate, only precipitated masses are obtained and not the true jelly. From all these facts, it is clear that zirconium sulphosalicylic acid forms a positively charged sol. Being a very impure system, the coagulating effect of chloride ions is masked by the protecting action of highly adsorbed potassium ions from potassium chloride, and hence a stabilisation is observed when the jelly is allowed to set in its presence. An abnormal dilution effect will also be observed in this case, i.e., if coagulation be effected by potassium chloride, the dilute sol would be found more stable than the concentrated sol. With sulphate and citrate ions, normal effects will be observed.

In many respects, the zirconium sulphosalicylic acid differs from mercuri-sulphosalicylic acid. The latter forms a negatively charged sol, whilst the former is a positively charged one. Zirconium sols and gels when evaporated to dryness do not pass into the colloidal state again when water is added. In this respect they are heat-irreversible. Mercuri- acid forms a typical organic jelly which exhibits a sort of

'melting' at a higher temperature, and takes more time to set when the temperature is raised. As has just been shown, the case with zirconium jelly is just the reverse of it.

Wo. Ostwald and Mertens (*loc cit.*) observed the 'dissolving' influence of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{CN}^-$ ,  $\text{CNS}^-$  ions on the colloidal phase of mercuri-sulphosalicylic acid. In presence of these ions, the colloidal nature of the sol at once disappears. However, in the case of zirconium sulphosalicylic acid, no such behaviour is observed.

The jelly of zirconium sulphosalicylic acid is only produced when sulphosalicylic acid is used and not when its neutral sodium salt. The medium must be highly acidic in order to produce a fine jelly. In the following table, the influence of alkali on the formation of this jelly has been illustrated.

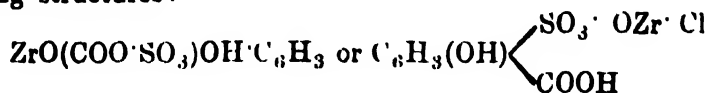
TABLE IV.

Zirconium oxychloride = 1 c.c. Sulphosalicylic acid = 2 c.c.  
Total volume = 5 c.c.

NaOH (N-6'84).	Time of setting	Nature of the jelly.
0.2 c.c.	7 hrs. 40 mins	Translucent
0.3	6 hrs.	Translucent
0.4	4 hrs.	Translucent
0.5	1 hr. 50 mins	Very opalescent
0.55	1 hr. 15 mins	Opaque
0.6	1 min	Opaque

Thus it would be seen that no jelly can be obtained in neutral or alkaline medium. It appears that zirconium sulphosalicylic acid is peptised to the colloidal form by the adsorption of hydrogen ions from the system. Sulphosalicylic acid is a fairly strong acid with a sufficiently high dissociation constant and so in strongly acidic solutions, only a very small part of zirconium sulphosalicylate may be supposed to be in equilibrium with zirconium hydroxide formed by hydrolysis.

Zirconium sulphosalicylic acid may be taken to possess one of the following structures :



Further work on this substance is in progress.



# **Presence of Formaldehyde in Rain and Dew and its Formation by Photo-oxidation of Organic Compounds and the Problem of Carbon Assimilation.**

BY N. R. DHAR AND ATMA RAM.

Recently we have shown (*Nature*, 1932, 130, 313) that all samples of freshly collected rain-water contain formaldehyde. The amount of formaldehyde in rain-water varies from 0.00015 to 0.001 g. per litre. We have ascribed the presence of formaldehyde in rain-water to its photo-formation from carbon dioxide and water vapour present in the air. We have also advanced the view that the first stage in this photo-formation of formaldehyde and in photosynthesis in plants is the photolysis of water into H and OH. The carbon dioxide is subsequently reduced by the atomic hydrogen formed by the photo-decomposition of water.

It might be argued that the formation of formaldehyde present in rain-water may be due to the electric discharge in the atmosphere during thunder storms. During the months of January, February, March and April, rain-water was collected and analysed every time there was a shower. On some of these days, electric discharge and thunder storms were observed. The amounts of formaldehyde present in rain-water are as follows :

Date.	Amount of formaldehyde per litre of rain-water.	Remarks.
Jan. 13, 1933	0.00055 g.	Accompanied with thunder storm
15	0.00055	No thunder storm
22	0.0004	Accompanied with thunder storm and hail storm
Feb. 25	0.0006	No thunder storm
Mar. 12	0.00045	Do
(2nd shower)		
13	0.0005	Accompanied with thunder storm
25	0.00075	Do
Apr. 12	0.0001	No thunder storm
14	0.0007	Accompanied with severe thunder storm and frequent lightning discharge
15	0.001	No thunder storm

From the foregoing observations it appears that the incidence of thunder storm does not increase the amount of formaldehyde present in rain-water. We have observed that the amount of formaldehyde present in rain-water is greater when the rainfall is preceded by some clear sunny days. Hence we are inclined to the view that formaldehyde in rain-water is obtained as a result of its photo-formation from carbon dioxide and water vapour.

Recently we have found that dew also contains formaldehyde. The amount of formaldehyde in dew is appreciably greater than that in rain-water. The amount of formaldehyde in most of the samples of dew collected so far was approximately 0.0015 g per litre. The formaldehyde in dew appears to come from the air in contact with grass, leaves, soil, etc.

It is well known that many organic substances on exposure to light forms formaldehyde. The production of formaldehyde by exposing chlorophyll under various conditions to light has been investigated by several plant physiologists.

The origin of this formaldehyde has not yet been satisfactorily explained. In order to throw light on this problem we have started a systematic investigation on the formation of formaldehyde by exposing solutions or suspensions of various organic substances to sunlight in presence of air. Dilute solutions of organic substances are exposed in beakers to sunlight for six hours and after exposure the solutions are distilled and the amount of formaldehyde estimated by the iodine method or by Schryver's reagent.

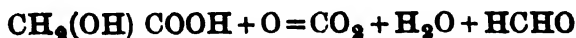
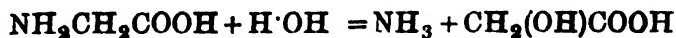
The organic substances investigated so far can roughly be classified into the following three groups according to the amount of formaldehyde formed from 100 c. c. of the solution.

A	B	C
Formaldehyde.	Formaldehyde.	Formaldehyde.
(0.0015—0.0007 g.).	(0.0006—0.0001 g.).	(0.0001—0.000015 g.)
Acetic acid	Pyruvic acid	Congo red
Glycine	Tartaric acid	Safranin
Methyl violet	Phloxine	Oxalic acid
Methylene blue	Aurine	Glucose
Acridine orange	Gallamine blue	Formic acid
Crystal violet	Laevulose	Arabinose

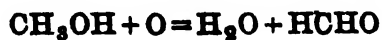
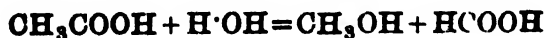


A	B	C
Malachite green	Galactose	Starch
Gentian violet	Aniline green	Inulin
Citric acid	Butyric acid	Cane sugar
Malic acid	Propionic acid	Stearic acid
Lactic acid	4:5'-Dihydroxyfuran	Pot. stearate
Glycerol	4-Hydroxy- 2'-methyl- 5'-isopropylfuran	Alanine
Acetone	4-Hydroxy- 2'-isopropyl- 5-methylfuran	Gelatine
Chlorophyll	4-Hydroxy- 3': 4'-pheny- lene(p-hydroxy)furan	Cholesterol
Glycogen	Sodium acetate	Leucine
	Sodium formate	Histidine
	Sodium butyrate	Phenylalanine
	Sodium propionate	Ergosterol
	Sodium oleate	

In the first group, the substances on exposure to light and air yield formaldehyde readily. By carrying on blank experiments in the dark and in the absence of air we have not observed any formaldehyde. When solutions of these substances are exposed to light and air, formaldehyde is formed mainly as a direct product of photo-oxidation. Thus in the case of glycine in presence of light and air the following reaction takes place :



In the case of acetic acid the probable mechanism of the reaction may be as follows :



We are of the opinion that with other substances of this group formaldehyde is a direct product of the photo-oxidation.

In the second group of substances the amount of formaldehyde formed from photo-oxidation is less than in the first class. It is difficult to state definitely whether the formaldehyde is a direct product of photo-oxidation or formed photochemically from carbon dioxide and water which are the products of oxidation of organic substances.

The formation of formaldehyde with the third class of substances is likely to be entirely due to the photosynthesis from carbon dioxide and water, produced in the photo-oxidation of the organic substances. From the researches of Palit and Dhar (*J. Phys. Chem.*, 1925, **29**, 925; 1928, **32**, 1263; 1930, **34**, 993; *Z. anorg. Chem.*, 1930, **191**, 150), it is evident that the energy-rich organic substances when exposed to light and air are partially oxidised to carbon dioxide and water. These freshly formed substances appear to be energy-rich and can undergo photosynthesis to formaldehyde in presence of light more readily than the ordinary carbon dioxide and water present in the atmosphere. That is why formaldehyde is more easily detected in the photo-oxidation of organic substances which liberate energy in their oxidation than in the case where ordinary carbon dioxide or bicarbonate solutions are exposed to sunlight. It will be of interest to note that almost all samples of acetic acid, glycerol, lactic acid, pyruvic acid, glycol, methyl alcohol, butyric acid, propionic acid and several other organic compounds kept in the store of our laboratories contain small amounts of formaldehyde formed from their slow photo-oxidation, and when exposed to air and light directly, the amount of formaldehyde is greatly increased.

It seems likely that the energy generated in the photo-oxidation of these organic substances applies a part of the energy for the photo-formation of formaldehyde. We are of the opinion that in nature, the photosynthesis that is taking place in the plants is aided by the energy obtained in plant respiration, which goes on as long as the plant lives. The ease with which formaldehyde or other energy-rich compounds are formed in plants is partly due to their getting a constant supply of energy from the oxidation of the food materials present in the plant. We have postulated that the most important chemical change in the formation of carbohydrates in plants and in the formation of formaldehyde in nature from carbon dioxide and water is the photolysis of water into H and OH. The amount of energy required to decompose a gram molecule of water into H and OH is the same as that necessary for the formation of a gram

mole of formaldehyde from carbon dioxide and water. These are highly endothermal changes requiring radiations of wave-length  $2550\text{\AA}$  (1,12,000 calories). In nature, however, photosynthesis takes place in visible light especially the red. We are of opinion that the energy derived from respiration in the plants already supplies a part of the energy necessary for the photosynthesis and thus rendering the photo-decomposition of water possible by longer wave-lengths. Although the adsorption of carbon dioxide and water by the chlorophyll of the leaf may partially activate these substances, just as the adsorption of hydrogen and oxygen on a platinum or palladium surface renders them active, it appears to us that this activation of carbon dioxide and water by their adsorption on the leaf surface is less important than their activation by the adsorption of energy from respiration. These observations explain the difficulty of obtaining formaldehyde or carbohydrates directly from carbon dioxide, bicarbonates and water *in vitro*. In the presence of an exothermal chemical change, such as the photo-oxidation of carbohydrates or other organic substances, the photo-formation of formaldehyde from carbon dioxide and water vapour appears to be greatly facilitated. We have carried on numerous comparative experiments on photosynthesis *in vitro* by exposing to sunlight aqueous chlorophyll suspensions saturated with either carbon dioxide alone or a mixture of carbon dioxide and oxygen. Moreover, similar experiments have been performed with potassium bicarbonate solutions instead of carbon dioxide. In the majority of cases, slightly greater amounts of formaldehyde were obtained with a mixture of carbonic acid or bicarbonate solutions and oxygen than in the cases where the chlorophyll suspensions were exposed to light and air in the absence of carbonic acid or bicarbonate solutions. In some of his experiments Warner (*Proc. Roy. Soc.*, 1914, **87 B**, 378) obtained more formaldehyde by exposing chlorophyll films to light in presence of a mixture of air and carbon dioxide than in presence of air alone. From comparative experiments on the photo-oxidation of organic acids, Palit and Dhar have shown that under identical conditions, oxalic acid is more readily oxidised in presence of light than tartaric or citric acid. On the other hand, by exposing solutions of these acids, very small quantities of formaldehyde are obtained in the case of oxalic acid, whilst the amount of formaldehyde formed from citric acid is much greater. It appears, therefore, that formaldehyde obtained by exposing oxalic acid solutions to sunlight and air is not a product of direct

oxidation, as in the case of citric acid, but is produced photosynthetically from energy-rich carbon dioxide and water, which are products of its photo-oxidation. It is rather peculiar that formic acid and sodium formate solutions yield very small amounts of formaldehyde when exposed to light and air. Dilute solutions of malachite green, crystal violet, methylene blue, gentian violet, acridine orange and methyl violet yield formaldehyde readily when exposed to light and air. Most of these dyes also behave as antiseptics. It will be interesting to investigate this problem further in order to find out whether all antiseptic dyes yield formaldehyde on photo-oxidation and the formaldehyde produced is the real antiseptic.

In this connection it will be worth while noting that formaldehyde is obtained even in the dark by treating carbonic acid or bicarbonate solutions with metals like magnesium, cerium, iron, etc. (Compare Dhar and Atma Ram, *Nature*, 1982, 129, 208). Recently we have been able to show that small amounts of formaldehyde are obtained by treating bicarbonate solutions with yellow phosphorus. In these cases the amount of formaldehyde formed is greater in light than in the dark. It appears that the energy-rich hydrogen produced by the action of the metals on water is capable of reducing the bicarbonate ion or carbonic acid to formaldehyde even in the dark, aided by the energy produced by the reaction of the metals on carbonic acid and bicarbonate solutions.

Now the question arises, can carbohydrates be obtained in plants even in the absence of light? It seems to be definitely settled that protein synthesis in plants can take place even in the dark in presence of carbohydrates, which undergo metabolism. It appears, that the synthesis of protein is possible when energy is supplied from the oxidation of carbohydrates without the addition of solar energy. From experiments carried on in these laboratories *in vitro*, by exposing solutions of formaldehyde and ammonia to sunlight in presence of different catalysts, we have come to the conclusion that there is less likelihood of the production of amino-acids and alkaloids than the formation of pyridine, piperidine, etc., due to the absence of carbohydrates, which are formed very slowly from formaldehyde *in vitro* even in presence of light. Recently we have been able to obtain evidence of the formation of amino-acids by exposing solutions of formaldehyde, glucose and ammonia or nitrite and catalysts like  $\text{TiO}_2$ ,  $\text{ZnO}$ , etc., to sunlight. Without using any catalyst we have been able to obtain evidence of amino-acids by the "ninhydrin"

test on exposing solutions of glucose, galactose or laevulose with potassium nitrate to sunlight.

Moreover, it appears that protein formation in plants is likely to be facilitated by the presence of fats, which yield glycerol readily. It has been shown by Dhar and collaborators that reducing sugars and formaldehyde are obtained by exposing glycerol to sunlight. Recently we have observed that reducing sugars are obtained by exposing solutions of tartaric acid and other hydroxy organic acids to light. Hence the presence of tartaric acid or other hydroxy organic acids may also favour the formation of proteins in plants, and these proteins appear to undergo oxidation very readily in plants, animals and *in vitro* in presence of light with the liberation of energy. Many plant physiologists have attempted to connect respiration with photosynthesis. Thus Spöhr ("Photosynthesis," 1926, p 143) states "Also, the light green varieties had a lower rate of respiration than the normal plants, though there was no direct parallelism between respiration and chlorophyll content. A closer relationship seems to exist between the rate of photosynthesis and that of respiration." Again on page 164, it is stated "Respiration is an important internal factor affecting photosynthesis, in addition to the chlorophyll content and the number of chloroplasts. The exact manner in which these two processes of respiration and photosynthesis may be linked is still an open problem." "Thus, while it is evident that there is no parallelism between chlorophyll content and rate of photosynthesis, the quotient respiration-photosynthesis is more constant. This quotient for the light green varieties was found to be as follows:

$$\begin{aligned} \text{Ptelea} &= 1.77, \text{ Catalpa} = 1.72, \text{ Mirabilis} = 2.0. \\ \text{Ulmus} &= 2.0, \text{ Populus} = 2.1. \end{aligned}$$

A correlation between respiration and photosynthetic rates was also noticed by Miss. Henrici (Inaug. Diss. Basel, 1918). She has observed in a study of alpine and lowland plants that those plants which had a high photosynthetic rate also had a high velocity of respiration and *vice versa*. Boysen-jensen (*Bot. Tidsskrift*, 1918, 36, 219) has also reported that plants which have a high rate of respiration also have a high velocity of photosynthesis. Similar results have also been obtained by Spöhr and McGee (*Carnegie Inst. Wash. Publ.*, 1928, No. 825, pp. 76-98).

From the view points discussed in this paper, it will be evident that the greater the respiration in a plant, the greater is the possibi-

lity of a supply of energy for photosynthetic purposes. In a recent communication (Dhar, *Bull. Acad. Sci. U. P.*, 1933, 2, 141) the importance of respiration in plant life has been emphasised and it has been concluded that respiration appears to be the more fundamental reaction in plants and is more important to plant life than photosynthesis, which predominates in plants only under restricted conditions of temperature and light intensity. The factor which really controls plant life is its respiratory or metabolic activity. As all plant processes depend on the energy available from respiration, which is the most vital reaction in plant life as much as in animal life, photosynthetic activity can not proceed without respiration taking place in the plant and hence without the presence of oxygen, which supports respiration in both the plant and animal kingdom. Because want of oxygen is detrimental to respiration, it is also harmful to photosynthesis. Consequently the classical experiments of Bous-singault (1868) and Pringsheim (1887), showing that in an atmosphere of hydrogen, nitrogen, carbon dioxide or methane, plants lose the power of photosynthesis, are easily explained, because in presence of these gases, oxygen respiration stops and the supply of energy necessary for the partial activation of carbonic acid and water is not available for the plant. It appears, therefore, that besides light, carbon dioxide, moisture and chlorophyll, energy from respiration is also necessary for photosynthesis.

Just as photosynthesis *in vitro*, that is, the formation of formaldehyde from exposing solutions of carbonic acid to sunlight, is exceedingly difficult in the absence of an exothermal chemical reaction taking place along with it, carbon assimilation in plants is also practically impossible in the absence of a supply of energy available from respiration. Moreover, it is well known that atmospheric nitrogen can only be fixed by some bacteria when supplied with energy from carbohydrate oxidation or another suitable exothermal oxidation reaction. In experiments *in vitro*, very little formaldehyde should be expected to form from carbonic acid or bicarbonate solutions on exposure to sunlight, because in sunlight short wave ultraviolet rays exist in small amounts. On the other hand, in presence of manganese and ferrous salts, we have been able to detect small quantities of formaldehyde frequently. This is because of the fact that these salts absorb visible light and also they are oxidised to the trivalent condition in presence of air and this exothermal chemical change supplies a part of the energy required for photosynthesis.

Hence it is easier to obtain formaldehyde or any other energy-rich compound from carbonic acid or bicarbonate solutions on exposure to light when a suitable exothermal reaction is made to take place in the same system along with the photosynthetic reaction.

In the case of the presence of formaldehyde in rain-water, we have explained its generation from photosynthesis of carbonic acid in higher altitudes where ultraviolet radiations of wave-length nearing  $2550\text{\AA}$  are available. The following appears to be the important steps in carbon assimilation :

1. Partial activation of carbon dioxide and water at the leaf surface due to their adsorption by chlorophyll and other plant pigments. It seems that chlorophyll and carotinoids present in the leaf act as photosensitisers and as reducing agents in the photo-reduction of carbonic acid.

2. Further activation of the adsorbed carbon dioxide and water by the absorption of a part of the energy available from respiration and the oxidation of carotin and the formation of activated carbon dioxide and water as products of respiration.

3. Absorption of light by chlorophyll and other pigments and the dissociation of activated water molecules in the leaf surface into H and OH and the reduction of activated carbon dioxide molecules to formaldehyde by the atomic hydrogen produced from the photolysis of water. The amount of energy required to decompose a gram mole of water into H and OH is the same as that necessary for the formation of a gram mole of formaldehyde from carbon dioxide and water.

4. The polymerisation of formaldehyde to reducing sugars.

5. The formation of hydrogen peroxide from OH and the rapid decomposition of  $\text{H}_2\text{O}_2$  into water and oxygen on the leaf surface.

The polymerisation of formaldehyde *in vitro* to reducing sugars is an exceedingly slow process even in presence of light. We have shown that it is accelerated by ferric salts. Moreover, it is known that in presence of alkali, reducing sugars are formed from formaldehyde. Light accelerates this reaction. How the formaldehyde formed on the leaf surface undergoes rapid polymerisation is still unknown.

Usher and Priestly (*Proc. Roy. Soc.*, 1906, 77 B, 369) Thurnberg (*Z. physikal. Chem.* 1924, 106, 305), Weigert (*Z. physikal. Chem.*, 1928, 106, 813; *ibid.*, 1924, 109, 79) and others have postulated the formation of  $\text{H}_2\text{O}_2$  in photosynthesis and its decomposition by

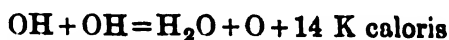
enzymes like catalase, etc. By exposing chlorophyll to light and air *in vitro*, Wager (*Proc. Roy. Soc.*, 1914, 87 B, 886), Warner (*loc. cit.*) and others have produced evidence in favour of hydrogen peroxide formation.

In recent years, the problem of the formation of hydrogen peroxide from OH radicals has been investigated. Frankenburger and Klinkhardt (*Trans. Faraday Soc.*, 1931, 27, 431) conclude that two water molecules are produced for each  $H_2O_2$  molecule formed in the combination of hydrogen and oxygen initiated by photochemically generated hydrogen atoms, and that the formation of  $H_2O_2$  is independent of temperature and the OH radicals must be relatively stable and require no energy for their activation in hydrogen peroxide.

From the measurement of the ultraviolet absorption spectrum of hydrogen peroxide, Urey, Dawsey and Rice (*J. Amer. Chem. Soc.*, 1929, 51, 1371) have concluded that for every absorbed light quantum two hydroxyl radicals are formed as follows :



On the other hand, Bonhoeffer and Person (*Z. physikal. Chem.*, 1931, 14 B, 1) are of opinion that free OH radicals react chiefly according to the following equation :



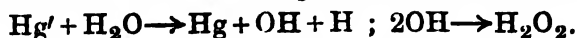
The life period of the free OH radicals is of the order of  $10^{-3}$  second. Moreover, von Elbe (*J. Amer. Chem. Soc.*, 1933, 55, 62) does not support the reaction mechanism of Frankenburger and Klinkhardt involving the recombination of two OH radicals to form hydrogen peroxide. According to Bates and Salley (*ibid.* p. 110) hydrogen peroxide is the sole product of the mercury sensitised hydrogen oxygen reaction.

Ultraviolet light causes the decomposition of water into its elements. According to Tian (*Compt. rend.*, 1913, 156, 1068) water is photochemically decomposed by extreme ultraviolet radiations. Coehn and Grote (*Nernst-Festschrift, Halle, 1912, p. 136*) have reported that a stationary state is reached between water and its elements by the action of ultraviolet light.

Senftleben and Behren (*Z. physik.*, 1926, 37, 529) have obtained only hydrogen as the gaseous decomposition product in the photosensitised decomposition of water vapour in presence of mercury and



have suggested that the reaction proceeds in the following steps:



Taylor and Bates (*J. Amer. Chem. Soc.*, 1927, **49**, 2488) have reported the production of 73%  $\text{H}_2$  and 27%  $\text{O}_2$  in the mercury-sensitised photo-decomposition of water.

It appears that the photolysis of the activated water molecules into H and OH on the leaf surface due to the absorption of light by chlorophyll and carotinoids resembles the cases of the photo-sensitised decomposition of water investigated *in vitro*.

#### SUMMARY.

(1) The amount of formaldehyde in rain-water does not increase with the incidence of thunder storms. Hence electrical discharge in the atmosphere does not seem to form formaldehyde from carbon dioxide and water vapour.

(2) Dew contains appreciable amounts of formaldehyde. The quantity of formaldehyde is greater in dew than in rain-water.

(3) When solutions of organic substances like acetic acid, citric acid, glycine, malic acid, lactic acid, glycogen, acetone, etc., are exposed to sunlight and air, formaldehyde is readily formed.

(4) Dyes like malachite green, methyl violet, methylene blue, etc., also form formaldehyde readily on photo-oxidation. Tartaric acid, butyric acid, propionic acid and some dyes form smaller quantities, whilst oxalic acid, formic acid, glucose, cane sugar, starch, histidine, etc., produce very small amounts of formaldehyde from photo-oxidation.

(5) It is believed that the formaldehyde formed in the first group of substances is a direct product of the photo-oxidation, whilst with oxalic acid, starch, glucose, etc., formaldehyde is obtained from the photosynthesis of the energy-rich carbon dioxide and water produced by photo-oxidation.

(6) It seems likely that the energy generated in the photo-oxidation of organic compounds supplies a part of the energy required for the photo-formation of formaldehyde. In nature, the photosynthesis that takes place in plants is aided by the energy obtained in plant respiration.

(7) There is an intimate relation between respiration and photosynthesis in the plant kingdom, because photosynthesis can not proceed without the energy available from respiration for the partial

activation of carbon dioxide and water vapour. The need of the presence of oxygen in photosynthesis is also explained from the same point of view.

(8) It is easier to obtain formaldehyde or any other rich compound from carbonic acid or bicarbonate solutions on exposure to light when a suitable exothermal reaction is taking place in the system along with the photosynthetic reaction.

(9) A theory of carbon assimilation in the plants is advanced from the view of the partial activation of carbon dioxide and water by the absorption of a part of the energy available from respiration. Absorption of light by chlorophyll and other pigments leads to the dissociation of the activated water molecules on the leaf surface into H and OH and this appears to be the most important photochemical reaction in carbon assimilation. The atomic hydrogen produced reduces the carbonic acid.

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*Received May 15 1933.*

## Decomposition of Hydrogen Peroxide by Potassium Ferro- and Ferricyanides.

By B. S. SRIKANTAN AND A. RANGA RAO.

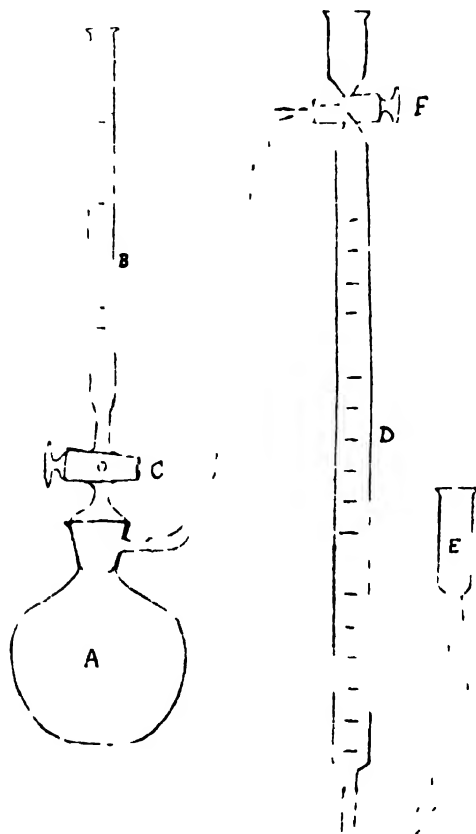
Kistiakowsky (*Z. physikal. Chem.*, 1900, **35**, 431), finds that the decomposition of hydrogen peroxide in the presence of a few drops of a mixture of solutions of yellow and red prussiate of potash is greatly accelerated by previously exposing the mixture to light. The exposure, however short it might be, had a pronounced effect in that the activity continued long after the illumination had ceased. The activity is attributed to the formation of a new catalyst by the action of light and not to any photochemical after-effect. This presents a peculiar and an interesting reaction in that the time of exposure of the mixture, however short it might be, of yellow and red prussiate to light, does not seem to have any appreciable difference in the final effect. Hence a systematic examination of the decomposition of hydrogen peroxide by yellow and red prussiate of potash in dark and in light, seemed to us desirable.

### EXPERIMENTAL.

Kistiakowsky (*loc. cit.*) followed the reaction by titrating definite amounts of the reaction mixture from time to time with dilute permanganate and after making a small, but rough correction for the amount of ferrocyanide taken, took the titre value as a measure of hydrogen peroxide still undecomposed in solution. This difficulty is eliminated in the following paper by finding out the amount of hydrogen peroxide decomposed by measuring the volume of oxygen evolved from time to time. The reaction was allowed to go on to completion for more than 24 hours. The total amount of oxygen was noted as infinity reading and from this the original concentration of hydrogen peroxide known. A small volume of gas that is dissolved in the liquid is not taken into account. This does not make any great error in the velocity coefficients since under the conditions of the experiments described here, it does not amount to more than 0.3 c.c. on the whole.

Chemically pure ferro- and ferricyanides of potash were used; fresh solutions were always made before any set of experiments. The hydrogen peroxide used throughout was of Schering-Kahlbaum suitably diluted.

FIG. 1.



The apparatus consists a reaction vessel A, connected to a graduated 10 c.c. pipette B, and capable of communicating with a nitro-meter burette D and levelling tube E through a side hole in the ground joint at the neck of the vessel. In most of the experiments 5 c.c. of suitably diluted hydrogen peroxide was placed in the reaction vessel and 10 c.c. of ferro- or ferricyanide of potash solution were taken in the pipette. The nitro-meter burette was filled with water and the three way tap F was turned to be in connection with the vessel A and to the atmosphere. The reaction vessel with the hydrogen peroxide solution was placed in an electrically controlled thermostat (correct to  $\pm 0.05^\circ$ ) so that it was immersed in water up to the neck. Time was allowed for the flask and its contents

to attain the temperature of the bath. Then 5 c.c. of the solution from the pipette was allowed to run into the flask along the sides of the vessel and thus allowed to mix without shaking and the tap F was turned quickly to connect the reaction vessel and the measuring burette. The time was noted and the volume of gas in the burette at atmospheric pressure was read off. The decomposition was followed by the amount of oxygen collected at atmospheric pressure, from time to time.

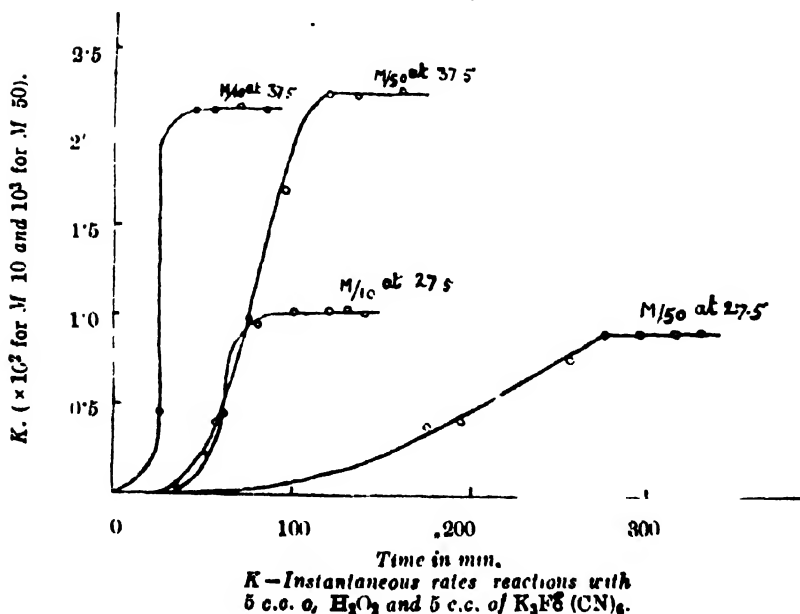
Care was taken not to expose the reaction mixture or the original solution to the action of light, except when it was so desired.

*Experiments with Potassium Ferrocyanide.*

Experiments were conducted with 5 c.c. of hydrogen peroxide solution and 5 c.c. of  $M/10$ -potassium ferrocyanide solution at  $25^\circ$ . Reproducible data were obtained, but the results were too complicated to be represented by the ordinary velocity equations. It appears that the reaction is not one of simple decomposition of hydrogen peroxide by ferro-cyanide but is complicated by subsidiary ones taking place as well. The following possibilities suggest themselves.

- (1) Decomposition of  $H_2O_2$  by ferrocyanide.
- (2) Oxidation of ferrous ion to ferric state by  $H_2O_2$ .
- (3) Decomposition of  $H_2O_2$  by ferri-cyanide formed.
- (4) Enhancement of reaction (1) by the inductive action of (2).

FIG. 2.



### Experiments with Ferricyanide.

Since the speed of the reaction is measured by the rate of evolution of oxygen from the liquid, it would be incorrect to calculate the velocity constant from the beginning by the application of the usual formula. Hence the instantaneous rates and the velocity coefficients were calculated at each point in the course of the reaction. For a unimolecular reaction it is given by

$$dx/dt \times 1/C_m,$$

TABLE I.

Time min in.	0	5	10	30	60	80	100	120	130	140	$\infty$
Burette reading in c.c.	0.5	0.5	0.5	0.5	2.8	5.4	7.9	9.9	10.7	11.4	18.6
Conc. of $\text{H}_2\text{O}_2$ in terms of c.c. of $\text{O}_2$	18.1	..	...	...	15.8	13.2	10.7	8.7	7.8	7.1	...

[illegible]

### TABLE II.

[illegible]

TABLE III.

$\text{H}_2\text{O}_2 = 5$  c.c.  $M/10\text{-K}_3\text{Fe}(\text{CN})_6 = 10$  c.c. Temp. =  $27.5^\circ$ .

Time in min.	0	40	60	80	100	120	140	150	160	180	200	220	
Burette reading in c.c.	2.0	2.0	2.0	2.0	4.1	6.0	8.6	9.65	10.60	12.20	13.35	14.40	18.5
Conc. of $\text{H}_2\text{O}_2$ in terms of c.c. of $\text{O}_2$	16.5	...	...	..	...	14.4	12.5	9.9	8.85	7.9	6.3	5.15	4.1
Instantaneous rates				...	...	0.0116	0.0112	0.0111	0.0112	0.0101	0.0114	...	
											mean	0.0111	

It appears that there is an initial disturbance after which the velocity coefficients are constant. The reaction is unimolecular and does not depend on the initial concentration of the hydrogen peroxide. The initial period consists of two definite portions; a short one where there is no evolution of gas followed by another period of gradually increasing rate of chemical transformation, till the regular velocity coefficients are obtained. The first one corresponds to a 'pseudo' period of induction as is usually observed in measurements of this type where the gas is retained by the liquid depending on its saturation capacity (cf. Veley, *Phil. Mag.*, 1903 (vi) 6, 271; Marchand, *Ann. chim. phys.*, 1873 (iv) 4, 30, 302). The regular period of induction corresponds to that when there is a slow and increasing rate of evolution of gas.

In order to verify this, experiments were performed with the same concentration of solutions but with different quantities so that the total volumes of the liquid were different. The results are described in Tables I, II and III. Other conditions being the same the total volume of the reaction mixture varies from 10 to 15 c.c. It is seen that the 'pseudo' period of induction depends on the volume of the liquid. Thus for a total volume of 10 c.c., the period is about 50 to 60 min., for 12.5 c.c. it is between 60 to 80 minutes and for 15 c.c. it is between 80 to 100 minutes.

Next experiments were performed with various concentrations of ferricyanide solution at  $27.5^\circ$ . and at  $37.5^\circ$ . The results are presented in Fig. 2 by means of graphs. The velocity coefficients at various times are plotted against the times. It is seen that the period of induction increases with dilution. With  $M/100$ , it was seen

that even after 6 hours working the period of induction was not passed. Experiments with  $M/500$  at  $37.5^\circ$ . showed that the reaction was immeasurably slow even after 2 days. Table IV shows that the product of the period of induction and concentration is fairly constant. At  $37.5^\circ$  the constant is about  $2/5$  its value at  $27.5^\circ$  corresponding to a temperature coefficient of the reaction velocity of about 2.5, described in the next section.

The data also shows the effect of dilution of potassium ferricyanide on the velocity coefficients.

TABLE IV.

Molar conc. of $K_3Fe(CN)_6$	..	0.1	0.05	0.02
Period of induction $\theta_1$ at $27.5^\circ$ .	...	61	122	275
.. .. $\theta_2$ at $37.5^\circ$ .	...	2.5	..	110
$\theta_1 \times C$	...	6.1	6.1	5.5
$\theta_2 \times C$	...	2.5	...	2.2

*N. B.* The values for the period of induction have been obtained from the graphs.

*Temperature coefficient.*—Experiments were performed at  $27.5^\circ$  and at  $37.5^\circ$  with concentrations of  $N/10$  and  $N/50$ -potassium ferricyanide. The summary of the results are given in Table V. The velocity coefficients after the initial period were always taken for the velocity constants

TABLE V.

Conc. of ferricyanide.	$K_{27.5}$	$K_{37.5}$	$K_{37.5}/K_{27.5}$
$M/10$	0.0101	0.0217	2.2
$M/50$	0.0009.3	0.00223	2.5

Thus the temperature coefficient of the reaction velocity is about 2.3.

*Effect of light.*—Kistiakowsky (*loc. cit.*) mentions the extraordinary sensitivity of this reaction to light, which persists even after the exposure has long ceased. He believes that it is due to the formation of a new catalyst in the presence of light and which catalyst is of



a colloidal nature. Two samples *M*/10 solutions of ferricyanide were exposed to bright sun light at midday, one for 5 minutes and the other for 80 minutes. The solutions were well cooled to 27.5° and experiments were conducted with them. The results are given in Tables VI and VII. The reaction starts at once and proceeds rapidly. It is clear that the only effect of such a treatment is to eliminate the period of induction. The velocity coefficients in both the cases were the same and the value is actually lower (about a third) than that obtained before exposing the solution to light. However, Kistia-kowsky failed to notice the period of induction, described here. So it is obvious that he has been comparing these values with the reaction rates during the period of induction; At such concentrations as he worked with, it is likely that the period of induction persists for many hours.

TABLE VI.

$H_2O_2 = 5$ c.c.	$M/10-K_3Fe(CN)_6 = 5$ c.c.				Temp. = 27.5°.
	Time of exposure = 5 min.				
Time in min.	0	60	92	123	∞
Burette reading (c.c.)	4.2	14.2	18.2	21.2	34.2
Instantaneous rates	...	0.00669	0.00695	0.00668	
				Mean 0.00674	

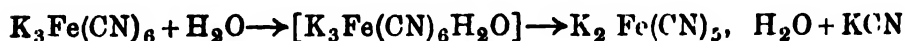
TABLE VII.

$H_2O_2 = 5$ c.c.	$M/10-K_3Fe(CN)_6 = 5$ c.c.				Temp. = 27.6°.
	Time of exposure = 30 min.				
Time in min.	0	82	101	160	∞
Burette reading (c.c.)	4	16.6	18.7	23.4	33.9
Instantaneous rates	..	0.00689	0.00680	0.00650	
				Mean 0.00673	

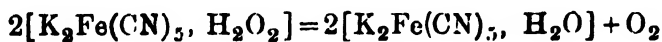
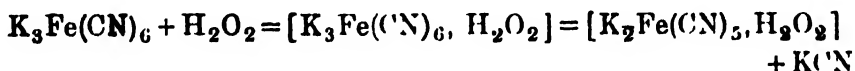
A solution of potassium ferricyanide, which is yellow, when exposed to light seems to undergo a gradual change. At first the solution becomes slightly greenish and in about half an hour it is dark blue. This appears to be colloidal in nature. On prolonged exposure prussian blue is precipitated, (cf. Friend, "Inorganic Chemistry" Vol. IX, Part II, p. 304; Vorländer, *Ber.*, 1913, 46, 181). Hence it appears that the elimination of the period of induction

after exposure to light is due to the formation of prussian blue (of a colloidal nature) which act as nuclei for the bringing together of  $\text{H}_2\text{O}_2$  and  $\text{K}_3\text{Fe}(\text{CN})_6$  by suitable adsorption.

*The Mechanism of the reaction.*—As there is a period of induction it is evident that the reaction proceeds through the formation of an intermediate complex. When a solution of  $\text{H}_2\text{O}_2$  is added to a solution of potassium ferricyanide, it is noted qualitatively that gradually the colour of the solution deepens and after some time, depending on the concentration of ferricyanide, changes from yellow to deep red. When the colour does not deepen further there is a brisk evolution of gas. On the analogy of Briggs (*J. Chem. Soc.*, 1920, 117, 1026) who shows that ferricyanide reacts with water to a slight extent as giving aquopentacyanoferrate;



it is possible that  $\text{H}_2\text{O}_2$  reacts more rapidly than water giving a hydrogen peroxide of pentacyanoferrate which decomposes giving aquopentacyanoferrate and oxygen as :



It is seen qualitatively that a solution of ferricyanide after treatment with hydrogen peroxide contains a greater quantity of potassium cyanide than the other for equal intervals of time. However in the absence of further evidence this is only a tentative explanation of the reaction.

#### SUMMARY AND CONCLUSIONS.

- (1) The decomposition of hydrogen peroxide by potassium ferrocyanide appears to be of a complicated nature.
- (2) The decomposition of hydrogen peroxide by potassium ferricyanide is unimolecular.
- (3) The reaction is attended with a period of induction which has been shown to be partly 'pseudo' (due to the retaining of the gas in solution) and partly 'real.'
- (4) The period of induction is inversely proportional to the concentration of ferricyanide and decreases with temperature

in the inverse ratio of the temperature coefficient of the reaction velocity.

(5) The temperature of the reaction velocity is about 2·3.

(6) Light does not accelerate the reaction as is supposed by Kistiakowsky (*loc. cit.*); light decomposes ferricyanide to prussian blue which acts as centres for the reaction to start, thus eliminating the period of induction.

(7) A mechanism of the reaction has been suggested on the basis of an intermediate complex formed between  $\text{H}_2\text{O}_2$  and  $\text{K}_3\text{Fe}(\text{CN})_6$ .

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## The Reactivity of the Chlorine Atom in the Benzene Nucleus.

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The reactivity of the halogen atom in a benzene nucleus under the influence of the nitro and other negative groups, has for a long time engaged the attention of chemists. It has been known that the nitro group is the only group that, in the absence of other groups causes really pronounced activation of the halogen atom, and that in comparison with the halogen in a halogeno-mononitrobenzene, *e.g.*, *o*-chloronitrobenzene, the halogen in other halogeno-monosubstituted benzenes, *e.g.* *o*-chlorocyanobenzene and *o*-chlorobenzoic acid, is practically inert. It would thus be understood why it is advantageous, for a proper comparison of the effects of substituents on the replacement of the halogen in an aromatic nucleus, to select such compounds as contain necessarily a nitro group in addition to the halogen atom and the activating substituent.

The object of the present investigation has been mainly the determination of the relative influence of (a) the nitro, (b) the cyano, and (c) the carboxyl groups on the reactivity of a chlorine atom adjacent to each of these groups in an aromatic nucleus. Attention has, therefore, been directed chiefly towards the condensations of (i) 1-chloro-2,4-dinitrobenzene, (ii) 1-chloro-2-cyano-4-nitrobenzene, and (iii) 1-chloro-4-nitro-2-benzoic acid (2-chloro-5-nitrobenzoic acid), all of which contain a nitro group in addition to the activating substituent, with the following compounds: aniline, *o*-, *m*- and *p*-toluidines, diethylamine, urea, sodium ethoxide, sodium methoxide and the sodium derivatives of ethyl malonate, ethyl acetoacetate, ethyl cyanoacetate, nitromethane and cyanoacetamide. Although several of these condensations have necessarily involved repetitions of previous work, the methods of experiment have often been modified with considerable advantage, and the results have helped in drawing certain clear and definite conclusions regarding the reactivity of the chlorine atom when it has either a nitro, a cyano or a carboxyl group adjacent to it and a further nitro group always fixed in the *para* position.

The condensation of 1-chloro-2:4-dinitrobenzene with aniline and *o*-, *m*- and *p*-toluidines has now been effected by merely warming a mixture of the components on the water-bath for 10-15 minutes in the case of aniline and about half an hour in the case of the toluidines (*vide* Reitzenstein, *J. pr. Chem.*, 1903, ii, 68, 251), the yields being practically quantitative.

Schöpf (Ber., 1890, 23, 3440), who prepared 2:4-dinitrodiphenylamine by heating 1-bromo-2-cyano-4-nitrobenzene and aniline to boiling for a long time, observed that under these conditions complications often set in, leading to the formation of nitroanilinobenzamide and nitroanilinobenzanilide. Again, Baudet (*Rec. trav. Chim.*, 1924, 43, 707) prepared 2-cyano-4-nitrodiphenylamine by mixing chloro-2-cyano-4-nitrobenzene and aniline in alcohol and heating under pressure in a sealed tube at 150° for 5 hours, no condensation being observed to take place on heating at a lower temperature, e.g., 130° for 2½ hours.

It is found now that the condensation between chloro-2-cyano-4-nitrobenzene and aniline is most quickly and conveniently effected by heating the substances together at 180°; the reaction is completed within ¾-1 hour and an excellent yield of 2-cyano-4-nitrodiphenylamine is obtained. Not only is the reaction completed in a much shorter time, but it is also kept well under control and does not permit the occurrence of any side-reactions. The same method has been successfully applied in the case of the toluidines also. The condensation, however, takes place only with *m*- and *p*-toluidines, *o*-toluidine not condensing with chlorocyanonitrobenzene even on heating at 200° for 2 hours (*cf.* Baudet, *loc. cit.*).

It may, therefore, be regarded as definitely established that the reactivity of the chlorine, at least with respect to primary aromatic amines, is less marked in chloro-2-cyano-4-nitrobenzene than in chloro-2:4-dinitrobenzene. Thus, whereas Mattaar (*Rec. trav. Chim.*, 1922, 41, 24, 103) succeeded in effecting the condensation between chloro-2-nitro-4-cyanobenzene and aniline by refluxing in alcohol for 1 hour, chloro-2-cyano-4-nitrobenzene is now found to react only on heating with aniline to 180° for about an hour, the same being the case with *m*- and *p*-toluidines. Again, chloro-2-cyano-4-nitrobenzene could not be condensed at all with *o*-toluidine and methylaniline even on heating for several hours at 200°, while Mattaar found the condensation of these two bases with chloro-2-nitro-4-cyanobenzene to be easily accomplished. These observations, therefore, are of consider-

able value in explaining the remarkable effect of exchanging the position of the two groups, *viz.*, cyano and nitro in chloro-2-cyano-4-nitrobenzene on the reactivity of the halogen.

The effect of the carboxyl group in the *ortho* position is shown by the fact that the condensation of 2-chloro-5-nitrobenzoic acid with aniline and the toluidines takes place with greater ease than in the case of chloro-2-cyano-4-nitrobenzene. The reaction is completed in the case of aniline and *m*- and *p*-toluidines by heating the reacting substances at 140° for 20-30 minutes, *o*-toluidine alone requiring to be heated to a somewhat higher temperature (160°) (*cf.* Locher, *Annalen*, 1894, 279, 275; also Kahn, *ibid.*, p. 270).

It may be concluded as a result of these experiments that the activating influence of the nitro, the cyano and the carboxyl groups on the replacement of halogen by means of the aromatic amines decreases in the order: nitro > carboxyl > cyano.

In this connection, attempts have also been made to condense chloro-2-cyano-4-nitrobenzene with the chloroanilines and the nitroanilines. The method employed has been to heat the substances at 190–200° for an hour or two. Of the three chloroanilines it is found that only *p*-chloroaniline condenses with chlorocyanonitrobenzene, giving 2-cyano-4-nitro-4'-chlorodiphenylamine (m. p. 282°). None of the nitroanilines could, however, be condensed with chlorocyanonitrobenzene. These observations serve admirably to illustrate the relative influence of a negative substituent, *e. g.*, Cl or NO<sub>2</sub>, in different positions in the aniline molecule in reducing the basicity and activity of the NH<sub>2</sub> group.

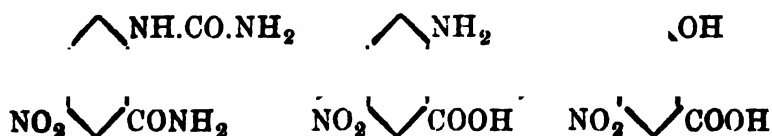
Diethylamine reacts very readily with chlorodinitrobenzene, the condensation taking place when the components are refluxed in alcohol for 20–30 minutes. The extreme case with which the reaction takes place is also observed by Romburgh (*Rec. trav. Chim.*, 1883, 2, 40) in the case of 1-bromo-2:4-dinitrobenzene. The condensation between diethylamine and chloro-2 cyano-4-nitrobenzene is also similarly accomplished by mixing the components in alcohol and boiling under reflux for 2–3 hours. In the case of 2-chloro-5-nitrobenzoic acid, however, reaction does not take place even on boiling for 4–5 hours. No better results are obtained by employing the sodium salt or the methyl ester of the acid for the condensation.

The reactivity of the halogen in these compounds towards urea has also been studied with interesting results. When chloro-2:4-

dinitrobenzene and urea are fused together 2:4-dinitroaniline is obtained. This method, for the replacement of the Cl by the  $\text{NH}_2$  group, is not, however, of general applicability, for such replacement does not occur with *o*-, *m*- or *p*-chloronitrobenzene.

The reaction proceeds on somewhat different lines in the case of chloro-2-cyano-4-nitrobenzene. When this compound is similarly heated with urea, a product is obtained melting at  $190^\circ$ . It is not 2-cyano-4-nitroaniline, m. p.  $209^\circ$ , (which has been prepared by Baudet by heating chlorocyanonitrobenzene with alcoholic ammonia under pressure), for it is not soluble in dilute or strong hydrochloric acid and can not be acetylated, whereby the absence of the  $\text{NH}_2$  group is proved. The product could not be hydrolysed by boiling with strong HCl, nor even by digesting with concentrated  $\text{H}_2\text{SO}_4$  at  $100^\circ$ , which renders the presence of a CN group doubtful. Analysis points to the probability of the compound being 2-uramido-5-nitrobenzamide. This constitution receives further support from the observation that the product of hydrolysis with moderately strong potash (15%) yields an acid (m. p.  $264^\circ$ ), which is found to be identical with 5-nitroanthranilic acid (m. p.  $263^\circ$ ) which has been prepared for comparison by direct nitration of anthranilic acid (the  $\text{NH}_2$  group protected by acetylation) with fuming nitric acid (*cf.* Rupe, *Ber.*, 1897, 30, 1097).

On hydrolysis by vigorous boiling with strong potash (20%) the product obtained is 5-nitrosalicylic acid (m.p.  $229^\circ$ ) the  $\text{NH}_2$  group of the 5-nitroanthranilic acid being substituted by hydroxyl, thus :



The formation of 2:4 dinitroaniline from 2:4-dinitrochlorobenzene and urea is now readily explained on the basis of the extreme reactivity of the halogen, which would appear to have easily been acted upon by the ammonia evolved from the urea. On the other hand, the lesser reactivity of chlorocyanonitrobenzene (1:2:4) would render such a replacement of chlorine with ammonia difficult, so that on prolonged heating the urea itself enters the molecule.



No definite product could, however, be isolated by condensing 2-chloro-5-nitrobenzoic acid or its methyl ester with urea, the major portion of the acid or ester being recovered unchanged.

With sodium ethoxide and sodium methoxide, again, chloro-2:4-dinitrobenzene condenses with extreme ease, the reaction being completed by refluxing for 20—30 minutes (*cf.* Cahours, *Annalen*, 1849, 69, 236; 1850, 74, 315; Willgerodt, *Ber.*, 1879, 12, 763; also Maikopar, *ibid.*, 1873, 6, 564).

The condensation between chloro-2-cyano-4-nitrobenzene and sodium ethoxide and methoxide is similarly effected by refluxing for 1-2 hours with sodium dissolved in the absolute alcohol, the products being identified with 1-ethoxy- and 1-methoxy-2-cyano-4-nitrobenzene which had been obtained previously by Blankema from 1-ethoxy- and 1-methoxy-2-amino-4-nitrobenzene respectively, by diazotisation and treatment with potassium cuprocyanide (*Chem. Weekblad*, 1908, 8, 789).

On similarly refluxing 2-chloro-5-nitrobenzoic acid, as well as its sodium salt, with sodium ethoxide and methoxide for 4-5 hours, the reaction does not proceed at all and most of the acid is recovered unchanged.

Thus, it has been found that with regard to these reagents as well as with diethylamine and urea, the halogen in chloro-2-cyano-4-nitrobenzene, while although less reactive than in chloro-2:4-dinitrobenzene, is replaced far more readily than that in 2-chloro-5-nitrobenzoic acid: the order with these reagents being  $\text{NO}_2 > \text{CN} > \text{COOH}$ .

From the foregoing experiments, therefore, the conclusion seems inevitable that, just as the order in which the different halogens are replaced depends upon the reagent used, as shown by the experiments of Luloffs (*Rec. trav. Chim.*, 1901, 20, 292) and Rheinlander (*J. Chem. Soc.*, 1923, 123, 3099), even so is the relative activating influence of the various negative groups on the halogen atom in an aromatic nucleus dependent largely on the nature of the reagents which are employed for substitution.

Again, if the results of the quantitative experiments of Mattaar and Baudet (*loc. cit.*) be taken into consideration, it must be conceded that with sodium ethoxide and methoxide, chloro-2-cyano-4-nitrobenzene reacts far more readily than chloro-2-nitro-4-cyanobenzene, whereas the reverse is found to be the case with the aromatic amines. This furnishes, therefore, a further illustration of the rule that the

nature of the particular reagent employed largely governs the relative influence of the activating substituents on the halogen atom.

Attention may in this connection be drawn to two interesting observations which seem to receive an explanation from this peculiarity. It has been found that sodium ethoxide reacts far more readily with *p*-nitrochlorobenzene than with *o*-nitrochlorobenzene and this observation is in line with that made by Rheinlander (*loc. cit.*), namely, that the speed of the reaction of sodium ethoxide with *p*-bromonitrobenzene is twice as great as that with *o*-bromonitrobenzene. The greater reactivity towards this reagent of chloro-2-cyano-4-nitrobenzene than of chloro-2-nitro-4-cyanobenzene appears thus to be readily explained as being due to the relative positions of the nitro group in these two compounds.

With regard to the reactivity of these substituted halogenated nitrobenzenes towards  $\beta$ -ketonic esters and allied derivatives, reference might be made to the work of Richter (*Ber.*, 1888, **21**, 2470), Reissert and Heller (*Ber.*, 1904, **37**, 4364), Borsche (*Ber.*, 1909, **42**, 602) and Borsche, Stackmann and Makaroff-Semljanski (*Ber.*, 1916, **49**, 2222) who have condensed sodioacetoacetic and sodiomalonic esters with substituted halogenated nitrobenzenes. This has now been extended to the study of the condensation of 1-chloro-2:4-dinitrobenzene, 1-chloro-2-cyano-4-nitrobenzene and 2-chloro-5-nitrobenzoic acid with the sodium derivatives of not only ethyl malonate and ethyl acetoacetate but also of ethyl cyanoacetate, nitromethane and cyanoacetamide. It is found, however, that reaction takes place only in the following cases: (a) chlorodinitrobenzene with sodiomalonic and sodioacetoacetic esters, (b) chlorodinitrobenzene and chlorocyanonitrobenzene with sodium cyanoacetamide. Even the use of catalysts like copper dust and copper acetate has not been found to bring about any reaction in the other cases.

The observations of Borsche, Stackmann and Makaroff-Semljanski (*loc. cit.*) are hereby corroborated. Thus, whereas these authors have condensed 1-bromo-2-nitro-4-cyanobenzene with sodiomalonic and sodioacetoacetic esters, it is now found that 1-chloro-2-cyano-4-nitrobenzene does not react with these esters, although repeated attempts have been made under different conditions to bring these into reaction. This difference in the behaviour of halogeno-2-nitro-4-cyanobenzene and of halogeno-2-cyano-4-nitrobenzene towards these reagents as well as towards the aromatic amines (*vide*

*supra*) serves, therefore, as one more example of the superior influence of the nitro group when adjacent to the halogen atom.

The condensations of chloro-2:4-dinitrobenzene and chloro-2-cyano-4-nitrobenzene with sodium cyanoacetamide have yielded very interesting results which are reserved for a future communication.

#### EXPERIMENTAL.

**1-Chloro-2-cyano-4-nitrobenzene.**—To 40 c.c. fuming nitric acid (*d* 1.5), well cooled in ice, *o*-chlorocyanobenzene (10 g.) (Montague, *Rec. trav. Chim.*, 1900, 19, 50) was gradually added with shaking. To the clear brown solution at 0° conc.  $\text{H}_2\text{SO}_4$  (40 c.c.) was added drop by drop with constant stirring. After standing an hour in the ice-bath, the liquid was poured into crushed ice, the precipitate collected, washed with 50% alcohol and crystallised from boiling alcohol as shining straw-yellow needles, m.p. 106°, yield 12.13 g. (*cf.* Borsche, *Ber.*, 1921, 54, 664).

**4-Chloro-3-cyanoaniline.**—To concentrated HCl (15-20 c.c.) in a small long-necked flask granular tin (8 g.) was added and the whole heated on a wire-gauze. When the evolution of hydrogen had become vigorous, chlorocyanonitrobenzene (3 g.) was gradually added with shaking, and the mixture boiled down to three-fourths the volume (15-20 minutes). On cooling, the clear yellow solution deposited a crystalline mass of the stannichloride. The mixture was diluted with a little water, made strongly alkaline with 50% caustic soda and directly extracted with ether. The product, obtained by evaporating the ether, crystallised from absolute alcohol in almost white needles, m.p. 133°, yield 2 g. (Found: N, 18.45.  $\text{C}_7\text{H}_5\text{N}_2\text{Cl}$  requires N, 18.38 per cent).

The *acetyl* derivative was prepared by warming 4-chloro-3-cyanoaniline (1 g.) with acetic anhydride (3.4 c.c.) to complete solution (10 minutes) and pouring into water; it crystallised from alcohol in small white needles, m.p. 190°, yield 1 g. (Found: N, 14.37.  $\text{C}_9\text{H}_7\text{ON}_2\text{Cl}$  requires N, 14.41 per cent).

4-Chloro-3-cyanoaniline could not be hydrolysed by strong  $\text{H}_2\text{SO}_4$  or HCl, the sulphate (m.p. 200-2°) or the hydrochloride (m.p. 224-26°)

\* the amine being the only products formed. Even on boiling with aqueous or alcoholic potash the substance remained unchanged.

**2-Chloro-5-nitrobenzoic acid** (*cf.* Rupe, *Ber.*, 1897, 30, 1099).—Crude *o*-chlorobenzoic acid (Kodak's technical, 20 g.) was slowly

treated with strong  $\text{H}_2\text{SO}_4$  (40 c.c.) when  $\text{HCl}$  fumes were given off and the solid slowly dissolved. Nitric acid ( $d$  1.4, 20 c.c.) was gradually added to this solution, cooled under the tap, with shaking and another 10 c.c. conc  $\text{H}_2\text{SO}_4$  added. It was warmed on the water-bath for an hour, cooled and poured into cold water (500 c.c.). The precipitate crystallised from boiling water as white prisms, m.p.  $164^\circ$ , yield 10-12 g.

The methyl ester was obtained by saturating with dry  $\text{HCl}$  at the ordinary temperature a solution of the acid (10 g.) in dry methyl alcohol (80 c.c.). The hot solution was cooled and again saturated with  $\text{HCl}$  gas and on leaving for 4 hours, the ester separated almost completely. The crystals were washed with 30 c.c. water and 5 c.c.  $\text{N-NaOH}$ . 10 G. of the pure ester (m.p.  $72^\circ$ ) were obtained.

#### CONDENSATIONS WITH AROMATIC AMINES.

##### A. Chloro-2:4-dinitrobenzene.

(i) *With aniline: 2:4-dinitrodiphenylamine.*—(a) A mixture of chlorodinitrobenzene (2 g.) and a slight excess of aniline (1.1 g.) was heated on the water-bath (10-15 minutes). The mixture was then dumped into cold water, the excess of aniline removed by washing with dilute  $\text{HCl}$  and the product crystallised from alcohol as shining orange needles, m.p.  $158^\circ$ , yield about 2.5 g.

(b) Chlorodinitrobenzene (2 g.) was gradually added with shaking to aniline (1.5 g.) when cooling was produced and a clear red liquid resulted. After allowing to stand for an hour, the mixture was worked up in the usual way, m.p.  $157-58^\circ$ , yield 2.8 g.

(ii) *With o-, m- and p-toluidines.*—The condensation of chlorodinitrobenzene (2 g.) with *o*-, *m*- and *p*-toluidine (1.3 g) was effected as above by warming on the water-bath for half an hour. The products obtained in the usual way were crystallised from glacial acetic acid: 2:4-dinitrophenyl-*o*-tolylamine (m.p.  $118^\circ$ ), 2:4-dinitrophenyl-*m*-tolylamine (m.p.  $160^\circ$ ) and 2:4-dinitrophenyl-*p*-tolylamine (m.p.  $135^\circ$ ) were obtained.

##### B. Chloro-2-cyano-4-nitrobenzene.

(i) *With aniline: 2-cyano-4-nitrodiphenylamine.*—A mixture of chlorocyanonitrobenzene (2 g.) and aniline (1.6 g., about  $1\frac{1}{2}$  mols.) was heated at  $180^\circ$  for  $\frac{1}{2}$ -1 hour. The clear dark-red liquid solidified on cooling and was freed from excess of aniline in the usual way

by triturating with very dilute HCl. The product crystallised from alcohol in clusters of lemon-yellow needles, m.p. 171°, yield 2 g. (Found: N, 17·76.  $C_{13}H_9O_2N_3$  requires N, 17·57 per cent).

(ii) *With p-toluidine: 2-cyano-4-nitro-4'-methyldiphenylamine.*—The condensation was effected in precisely the same manner as in the case of aniline by heating the mixture of chlorocyanonitrobenzene (2 g.) and *p*-toluidine (1·8 g.) in an oil-bath at 180–85° for an hour. The product, worked up as usual, crystallised from glacial acetic acid in shining yellow needles, m.p. 217°, yield 1·7 g. (Found: N, 16·93.  $C_{14}H_{11}O_2N_3$  requires N, 16·60 per cent)

(iii) *With m-toluidine: 2-cyano-4-nitro-3'-methyldiphenylamine.*—On repeating the experiment with *m*-toluidine exactly as in the previous case, 1·5 g. of the product, crystallising from alcohol in small pale green crystals, m.p. 140°, are obtained. (Found: N, 16·78.  $C_{14}H_{11}O_2N_3$  requires N, 16·60 per cent).

(iv) *With o-toluidine and methylaniline.*—The above experiment was done with *o*-toluidine and methylaniline, but there was no condensation, the chlorocyanonitrobenzene being recovered unchanged in each case. No better results were obtained even when the components were heated at 200° for 2 hours.

(v) *With p-chloroaniline: 2-cyano-4-nitro-4'-chlorodiphenylamine.*—The mixture of chlorocyanonitrobenzene (2 g.) and *p*-chloroaniline (1·9 g.) was similarly heated at 190–195° for 1 hour. The product, after treatment in the usual manner, crystallised from acetic acid in bright yellow needles (1·1 g.), m.p. 282°. (Found: N, 15·52.  $C_{13}H_8O_2N_3Cl$  requires N, 15·35 per cent).

### C. 2-Chloro-5-nitrobenzoic Acid.

(i) *With aniline: 2-anilino-5-nitrobenzoic acid.*—2-Chloro-5-nitrobenzoic acid (2 g.) and aniline (1·4 g.) were heated together at 140° for 20 minutes. The product was washed with dilute HCl and crystallised from acetic acid as pale yellow needles, m.p. 250°. (*cf.* Schopff, *loc. cit.*)

*2-Anilino-5-nitrobenzamide.*—2-Chloro-5-nitrobenzamide (2 g.) and aniline (1·4 g.) were heated together at 160° for half an hour. The product, purified in the usual manner, was crystallised from alcohol in shining yellowish-green needles, m.p. 190°, yield 1·7 g. (Found: N, 16·59.  $C_{13}H_{11}O_2N_3$  requires N, 16·84 per cent).

**Methyl 2-anilido-5-nitrobenzoate.**—Methyl 2-chloro-5-nitrobenzoate (2 g.) and aniline (1.4 g.) were heated together at 160° for 10-15 minutes. On cooling, the mixture solidified to a sludge of crystals, which became granular on stirring for a while with 40 c.c. N-HCl. This was taken in a mortar, powdered with a little methyl alcohol and 2N-NaOH (1 c.c.) added drop by drop, when the whole thing was transformed into a mass of golden yellow crystals. The product crystallised from alcohol in golden yellow flat needles, m.p. 100°, yield 1.6 g. (Found : N, 10.46.  $C_{14}H_{12}O_4N_2$  requires N, 10.29 per cent).

(ii) *With o-toluidine : 5-nitro-2-o-toluidinobenzoic acid*, (cf. Locher, *loc. cit.*) obtained in the usual way by heating together chloronitrobenzoic acid (2 g.) and o-toluidine (1.6 g.) at 160° for about half an hour, crystallised from alcohol in yellow needles, m. p. 254°.

(iii) *With p-toluidine : 5-nitro-2-p-toluidinobenzoic acid*, (cf. Kahn, *loc. cit.*) obtained by heating the components at 140° for 20 minutes, melted at 262°.

(iv) *With m-toluidine : 5-nitro-2-m-toluidinobenzoic acid*, prepared exactly as in the above case, crystallised from acetic acid in bright yellow needles, m. p. 256°, yield about 1.8 g. from 2 g. of chloronitrobenzoic acid. (Found : N, 10.52.  $C_{14}H_{12}O_4N_2$  requires N, 10.29 per cent).

#### CONDENSATIONS WITH DIETHYLAMINE.

**2:4-Dinitrodiethylaniline.**—To a solution of chlorodinitrobenzene (2 g.) in ethyl alcohol (10 c.c.) diethylamine (1 g.) was added and the solution refluxed on the water-bath for 20-30 minutes. On concentrating, the product crystallised out, m.p. 81°, yield 1.2 g. Romburgh (*loc. cit.*) obtained this product by leaving an alcoholic mixture of 1-bromo-2:4-dinitrobenzene and diethylamine undisturbed for several hours.

**2-Cyano-4-nitrodiethylaniline.**—Chlorocyanonitrobenzene (2 g.) was similarly boiled under reflux with diethylamine (1.2 g.) in absolute ethyl alcohol for 2-3 hours. The solution was concentrated and poured into water and the product crystallised from absolute alcohol in fine pale-yellow needles, m. p. 88°, yield 1.4 g. (Found : N, 19.41.  $C_{11}H_{13}O_2N_3$  requires N, 19.18 per cent).

## CONDENSATIONS WITH UREA.

**2:4-Dinitroaniline.**—Chlorodinitrobenzene (3 g.) was added in small quantities to molten urea (3 g.) at 160° with stirring. After heating for an hour the contents of the flask, when quite cold, were washed 3 or 4 times with warm water to remove excess of urea and the product crystallised from boiling water as bright yellow needles, m. p. 176°, yield about 2 g. (Found: N, 23.28.  $C_6H_5O_4N_3$  requires N, 22.95 per cent).

**2-Uramido-5-nitrobenzamide.**—Chlorocyanonitrobenzene (3 g.) and urea (3 g.) were similarly heated together at 165-170° for 2 hours. After washing with warm water, the product was extracted with acetone and the substance, obtained on evaporating acetone, crystallised from boiling water in small orange-yellow needles, m. p. 198°, yield 1.5 g. (Found: N, 25.35.  $C_8H_8O_4N_4$  requires N, 25.0 per cent).

2-Uramido-5-nitrobenzamide (5 g.) was heated with caustic potash (15%, 10-15 c.c.) just to boiling for half an hour, when ammonia was evolved. The clear liquid was acidified and the precipitate, after washing with a little hot water, crystallised from aqueous alcohol in golden-yellow needles, m. p. 264°. The product was identified with 5-nitroanthranilic acid prepared by the following method which was found to be more convenient and gave a purer product than that of Rupe (*loc. cit.*) who employed a mixture of nitric acid and sulphuric acids for the nitration. Acetyl anthranilic acid (1 g.) was added gradually to fuming nitric acid (d 1.5, 5 c.c.) with constant cooling. The clear liquid, after leaving for half an hour, was poured into water and the precipitate of 5-nitroacetyl anthranilic acid (m. p. 214°) was deacetylated by boiling with concentrated HCl for half an hour and the 5-nitroanthranilic acid crystallised from aqueous alcohol in shining yellow needles, m. p. 263°.

Hydrolysis of 2-uramido-5-nitrobenzamide by vigorous boiling with 20% caustic potash yielded 5-nitrosalicylic acid (m.p. 229°). *O*-, *m*- and *p*-chloronitrobenzene did not react with urea.

## CONDENSATIONS WITH SODIUM ETHOXIDE AND METHOXIDE.

**1-Ethoxy-2:4-dinitrobenzene** (m.p. 86°) and **1-methoxy-2:4-dinitrobenzene** (m. p. 89°), (*cf.* Willgerodt, *loc. cit.*, Malkopar, *loc. cit.*)

were obtained by refluxing chlorodinitrobenzene (2 g.) with sodium (0.25 g.) dissolved in absolute ethyl and methyl alcohol respectively for 20-30 minutes.

1-Ethoxy-2-cyano-4-nitrobenzene (m.p. 101°) and 1-methoxy-2-cyano-4-nitrobenzene (m.p. 128°) (*vide* Baudet, *loc. cit.*) were obtained when chlorocyanonitrobenzene (1.8 g) was added to sodium (0.25 g.) dissolved in absolute ethyl and methyl alcohol respectively and refluxed for 1-2 hours. They were recrystallised from aqueous alcohol. (Found: N, 14.51.  $C_9H_8O_3N_2$  requires N, 14.58 per cent) (Found: N, 15.8.  $C_8H_6O_3N_2$  requires N, 15.73 per cent). No reaction was found to take place when chloronitrobenzoic acid (either the free acid or the sodium salt) was similarly refluxed with sodium dissolved in absolute ethyl and methyl alcohol respectively for 4-5 hours, the unchanged acid being recovered in each case.

On condensing sodium ethoxide and *p*-chloronitrobenzene exactly as in the previous cases, the reaction proceeded normally with the formation of *p*-nitrophenetole, m.p. 57°. A by-product was also formed which melted at 154° and was identified with *pp'*-dichloro-azoxybenzene.

No definite product could, however, be isolated on repeating the experiment with *o*-chloronitrobenzene.

*Condensations with Sodiomalonic Ester, Sodio-acetoacetic Ester, etc.*

2:4-Dinitrophenylmalonic ester (m.p. 52°) and 2:4-dinitrophenyl acetoacetic ester (m.p. 83°) (*cf.* Reissert and Heller, *Ber.*, 1904, 37, 4364) were obtained by adding chlorodinitrobenzene to a solution of ethyl malonate and ethyl acetoacetate (2 g.) in alcoholic sodium ethoxide (0.25 g. sodium) and refluxing for 2-3 hours. The products were crystallised from alcohol.



## **Diamagnetism of Bismuth and Antimony in the Colloidal State.**

BY MULK RAJ VERMA AND RAM NARAIN MATHUR.

Soon after the publication of Vaidyanathan's work, (*Indian J. Phys.*, 1980, 5, 559), which showed that the diamagnetic susceptibility of bismuth, antimony and graphite decreases on powdering, Bhatnagar (*J. Indian Chem. Soc.*, 1980, 7, 957) pointed out that the absence of impurities in the form of oxide or sub-oxides of the elements in question, particularly bismuth and antimony, and the absorbed gases must be made sure of, before accepting any effect of mechanical colloidalisation on diamagnetic susceptibilities. Mathur and Verma (*Indian J. Phys.*, 1981, 6, 181) developed this view and showed that the original value of bismuth can be regained if the oxides are suitably removed. The same point was emphasised about antimony later (*Proc. Ind. Sci. Congress., Chem. Sec.*, 1982). Rao (*Indian J. Phys.*, 1981, 6, 241) claimed that below a definite size corresponding with the size of the macrocrystal\* a rapid change in the susceptibility of bismuth ensues. Vaidyanathan and others too have stressed the same point on the susceptibility measurements of chemically prepared gold (Vaidyanathan and Singh, *Nature*, 1981, 128, 802) and silver sols (Vaidyanathan and Puri, *ibid.*, 1982, 129, 170). It seems, however, that in trying to get rid of the oxide impurity, Rao has forgotten that impurities in the form of carbonates, bicarbonates, etc., can also be obtained if the powdering is done under water (Mellor, "Treatises on Inorganic Chemistry", Vol. IX, p. 626), as has actually been done by him. With a view to avoid contamination due to these impurities, bismuth has been reinvestigated, the powdering being done under liquid paraffin, for particle sizes much smaller than those reported in our communication already referred to. Antimony has also been investigated along the same lines as bismuth, as it also exhibits magnetic anisotropy. Another point of interest which made us undertake this work is that

Quoted by Rao,

antimony is capable of being oxidised very easily. It is very probable, therefore, that oxidation has a good deal to do with the observed decrease in the susceptibility obtained by Vaidyanathan and Rao (*loc. cit.*), for the lowest size ( $150\mu$ ) reached by the former is not so low as to be able to affect the lattice electrons encircling a larger number of atoms as put forward by Ehrenfest (*Physica*, 1925, 8, 388). The changes observed on powdering in the case of bismuth and antimony are capable of a satisfactory explanation on chemical grounds only as shown by the results of the investigation described below.

#### EXPERIMENTAL.

Bismuth was powdered in the first stages under liquid paraffin and later under benzene to check oxidation as much as possible. Particles were graded out into different sizes by shaking the paraffin-free powders with benzene and removing the layers settling down at different intervals of time. The sizes were determined by means of a Leitz high magnification power microscope and the magnetic susceptibilities by means of a torsional balance of the Curie-Wilson type. The powders were also investigated after removing the oxide impurity by means of tartaric acid and the values so obtained are placed in the last column of the following table for the sake of comparison.

TABLE I.

Substance.	Magnetic susceptibility $\times 10^{-6}$	
	Before removing the oxide.	After removing the oxide.
Bismuth	—1.27	
Coarse powder ( $1\mu$ — $1.2\mu$ )	—0.84	—1.27
Fine powder ( $0.7\mu$ )	—0.72	—1.233

Investigation on antimony was divided into the following parts:

1. Powdering the metal in air for different intervals of time and investigating the samples so obtained along with the coagula obtained by sparking between the metal electrodes under conductivity water,

2. Detecting and estimating the oxide purity.

3. Removing the oxide impurity and investigating the samples magnetically.

4. Powdering the metal under inert liquids to check oxidation and to reinvestigate the samples.

The results obtained under different heads are described below in the above order.

1. *Powdering the metal at different intervals.*—Antimony was powdered in a well-polished agate mortar and powdered samples were collected at different intervals of time. The coagulum was obtained by sparking between the metal electrodes and coagulating by exhaustive cataphoresis.

TABLE II.

Current=1 Amp. Initial reading on the torsion head=128°·0'.

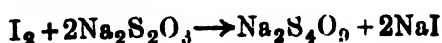
Substance.	Wt	Final reading.	Torsion given.	Magnetic susceptibility $\times 10^{-6}$ .	Particle size.
Water	0·1000 g.	238°·19'	110°·19'	-0·72	...
Capsule	1·7480	208°·48'	80°·48'	...	...
Antimony metal	0·1000	241°·3'	113°·3'	-0·812	...
Powder No. 1.	0·1000	231°·24'	103°·24'	-0·568	5·0 $\mu$
„ No. 2.	0·1000	229°·20'	101°·20'	-0·516	2·5
„ No. 3	0·1000	228°·42'	100°·42'	-0·499	1·5
„ No. 4	0·1000	228°·39'	100°·39'	-0·498	1·0
Coagula	...	...	...	-0·579	...

It is clear from the above table that the diamagnetism of antimony goes on decreasing with the particle size. The rate of decrease, however, becomes negligibly small when the particle size reaches 1·5 $\mu$ . Further powdering, therefore, appeared unnecessary. The smallest value for the diamagnetism of antimony obtained by Vaidyanathan is  $-0·586 \times 10^{-6}$ . The value for the last powder in the above table is a little less, but our value for the coagulum is considerably higher than that obtained by Vaidyanathan (*loc. cit.*).

2. *Detection and estimation of the oxides.*—The presence of the oxides of antimony in the powders was determined as follows and is based upon the well known fact that whereas antimony metal does not dissolve in dilute hydrochloric acid, all its oxides are soluble therein. A small amount of the powder was, therefore, boiled with dilute hydrochloric acid, filtered and the filtrate was tested for antimony by the usual test with hydrogen sulphide. In every case a thick orange precipitate of antimony sulphide was obtained, proving beyond doubt, that the samples contain the oxides of the metal as impurity. In order to estimate the amount of this impurity in the sample, an attempt was made to remove the oxide completely by boiling with hydrochloric acid. It was then discovered that the oxide is rather tenacious and leaves the metal with great difficulty and so even on successive boilings with dilute hydrochloric acid could not be removed completely. A direct estimation of the antimony content of the samples, by the method given below was, therefore, resorted to (Scott, "Standard Methods of Chemical Analysis", Vol. I). It is known that nitric acid oxidises antimony from trivalent to pentavalent type, which then reacts with potassium iodide to liberate iodine according to the reaction :



and this amount of iodine liberated can be estimated by titrating against sodium thiosulphate :



Equal quantities of the powders (0.1 g) were in each case, therefore, dissolved in a mixture of hydrochloric acid (10 c.c.) and concentrated nitric acid (1 c.c.). Excess of nitric acid was boiled off and the sides of the flask thoroughly rinsed with 1:1 dilute hydrochloric acid. The whole volume was made up to 60 c.c. by adding distilled water and 8 c. c. of 20 % potassium iodide solution. This was then titrated against standard thiosulphate solution, the end point being noted by the disappearance of the red colour from  $\text{CS}_2$  already added to the solution. For the success of experiment it was, however, necessary to keep the solution very cold during all this interval.

The concentrations of the various samples tried in terms of antimony are given below. The samples are the same as those tried in Table II.

TABLE III

Sodium thiosulphate soln. conc. = 0.09024N.

Substance	Wt.	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> soln.	Sb content	Sb in the samples.
Antimony	0.1000 g.	18.45 c c.	0.1000 g.	100.0%
Powder No. 1	0.1000	17.5	0.0948	94.8
" No. 2	0.1000	17.0	0.092	92.0
" No. 3	0.1000	16.8	0.0918	91.0
" No. 4	0.1000	16.77	0.0908	90.8
Coagula	0.1000	17.0	0.0920	92.0

From the data given in Table II it is clear that the diamagnetic susceptibilities of the powders tend to be constant when the particle size reaches  $1\mu$ . If this fall in diamagnetism is due to the impurity of the oxides in the powders, the antimony content of the samples should also tend to be constant at the particle size  $1\mu$ . This is exactly what is found to be, the antimony content of the powder No. 3 in the above table is very nearly the same as that of the powder No. 4.

3. *Removing the oxides from the powders and reinvestigating the samples so obtained magnetically.*—As given before, it is well known that whereas the metal itself does not dissolve in dilute hydrochloric acid, all its oxides are soluble therein. Hence in order to get rid of the oxides the powders were boiled with dilute hydrochloric acid and filtered and the process continued until the washings gave no test for antimony. The purified samples were then finally washed with extra pure acetone and left to dry in vacuum. When perfectly dry, they were reinvestigated magnetically and the results obtained are given in the Table IV. In order to facilitate comparison, the values of  $\chi$  for these samples before freeing them from the oxides are also given in the last column.

TABLE IV.

Substance.	Wt.	Final reading	Torsion given.	Magnetic susceptibility $\times 10^{-6}$ .	Magnetic susceptibility before removing the oxide. $\times 10^{-6}$ .
Antimony	0.1000 g.	242°.16'	114°.16'	-0.841	-0.812
Powder No. 1	0.1000	241°.57'	113°.57'	-0.834	-0.808
" No. 2	0.1000	241°.54'	113°.54'	-0.823	-0.816
" No. 3	0.1000	241°.0'	113°.0'	-0.810	-0.499
" No. 4	0.1000	240°.4'	112°.4'	-0.805	-0.498
Coagula				-0.814	-0.829

It is clear from the above table that the powders practically regain the value for metal crystals after being boiled with hydrochloric acid, in which the oxides of antimony are soluble. This crucial test leaves no room for doubt that the observed fall in the diamagnetism of antimony is almost completely due to the oxide impurity. The fact that the powders do not exactly regain the value for metal crystals can easily be accounted, for on a visual observation it is seen that the surface of antimony crystals loses its metallic lustre even on almost an instantaneous exposure to the atmosphere. At small particle size, the surface increases very considerably and obviously surface oxidation shall affect the results appreciably.

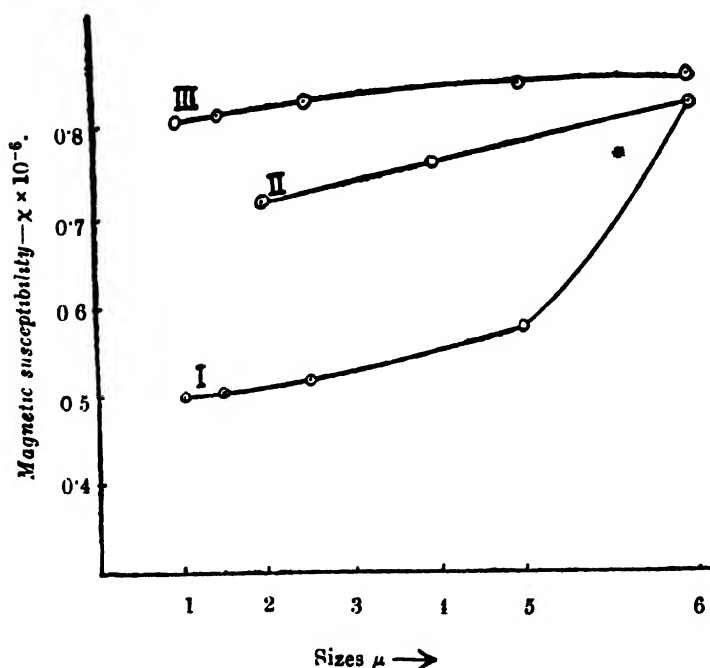
4. *Powdering under inert liquids.*—If the oxide is formed by powdering in air, it is obvious that much less of it shall be obtained if the powdering is done under an inert liquid. The samples, therefore, should be much more diamagnetic than those obtained in air for the same particle size. So the powdering was done under liquid paraffin and the samples so obtained were washed free of paraffin by means of ether and dried in vacuum. They were later on magnetically investigated and the results are given in the following table.

TABLE V.

Initial reading = $123^{\circ}0'$ .			Current = 1 Amp.		
Substance.	Wt.	Final reading.	Torsion applied.	Magnetic susceptibility $\times 10^{-6}$ .	Particle size.
Water	0.1000 g.	$254^{\circ}38'$	$131^{\circ}33'$	-072	...
Capsule	1.7480	$219^{\circ}0'$	$96^{\circ}6'$	...	...
Antimony metal	0.1000	$257^{\circ}18'$	$134^{\circ}18'$	-0808	...
Powder No. 5	0.1000	$255^{\circ}8'$	$132^{\circ}8'$	-0758	...
.. No. 6	0.1000	$253^{\circ}18'$	$130^{\circ}18'$	-0714	$2\mu$

For the sake of comparison all the values of  $\chi$  that have been obtained are plotted against the particle size in the accompanying graph. The curve for the samples powdered under liquid lies above that obtained for the samples powdered in air, and the one for the samples washed free of the oxide lies almost parallel to the  $\chi$  axis, which

proves beyond doubt that the observed fall in the diamagnetism is due to the formation of oxide impurity.



I—Sb powders ; II—Sb powdered under water ; III—Sb (oxide removed).

#### SUMMARY AND DISCUSSION OF RESULTS

The results arrived at in the course of this investigation lend further support to the view put forward by Bhatnagar and developed by us in our previous communication, that practically the whole of the observed fall in the diamagnetism in the case of these metals is due to the formation of oxide impurities formed during the process of powdering employed for colloidalisation. Bismuth metal, as shown in Table I acquires almost completely the regulus value of susceptibility after a complete removal of the oxide impurities. Antimony also shows the same value in the finely divided state as in the massive condition. We might, therefore, conclude that the magnetic susceptibility in the case of these metals is practically independent of the particle size. This view has recently been supported by the work of Lane (*Nature*, 1932, 130, 999) in the laboratory of Professor Gerlach, who has shown that the mass susceptibility of bismuth in the form of thin films ranging from  $0.2\mu$  to  $15\mu$  has almost the same value as the metal itself. It seems, therefore, that there are still some impurities

left behind in Rao's samples, (*loc. cit.*) which are responsible for a persistently low value obtained by him. Another possible explanation is suggested by the recent work of Seemann and Kussmann (*Naturwiss.*, 1981, 19, 809) to explain the effect of cold working on the susceptibility. The process of powdering may be regarded as akin to cold working and in this process probably some ferromagnetic impurities crystallise out resulting in a decrease in the magnetic susceptibility. Melting the coagula as Rao (*Nature*, 1932, 129, 545 ; *Indian J. Phys.*, 1932, 7, 35) has done, would render these impurities inactive resulting in an increase in diamagnetism. As suggested by Lane this point may be checked up by measuring the susceptibility of each powder under the influence of various field strengths which would be able to give us a valuable information with regard to the above point.

Absorption and adsorption of gases have recently been shown to affect profoundly the magnetic properties of  $\alpha$ -manganese and it is just possible that this phenomenon plays a very important role at vanishingly small particle sizes in the case of these metals and it may be that the increase in susceptibility obtained by Rao on melting the coagula is due to the liberation of entrapped gases. Further work has therefore been undertaken in this laboratory in connection with the behaviour of metals at low particle sizes and the results arrived at shall be submitted for publication shortly.

Our thanks are due to Prof. S. S. Bhatnagar for his very kindly helping us in the course of this investigation and to the Punjab Chemical Research Fund for the award of scholarships to the authors which has made this work possible.

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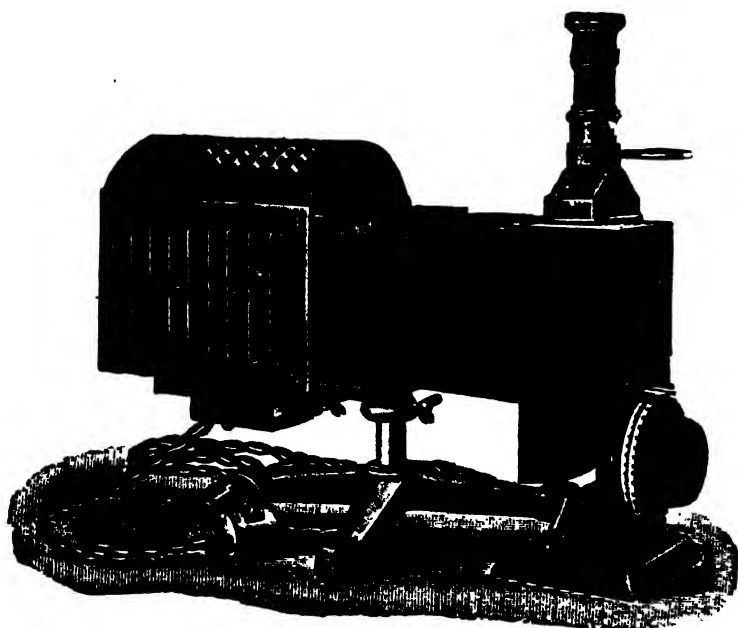
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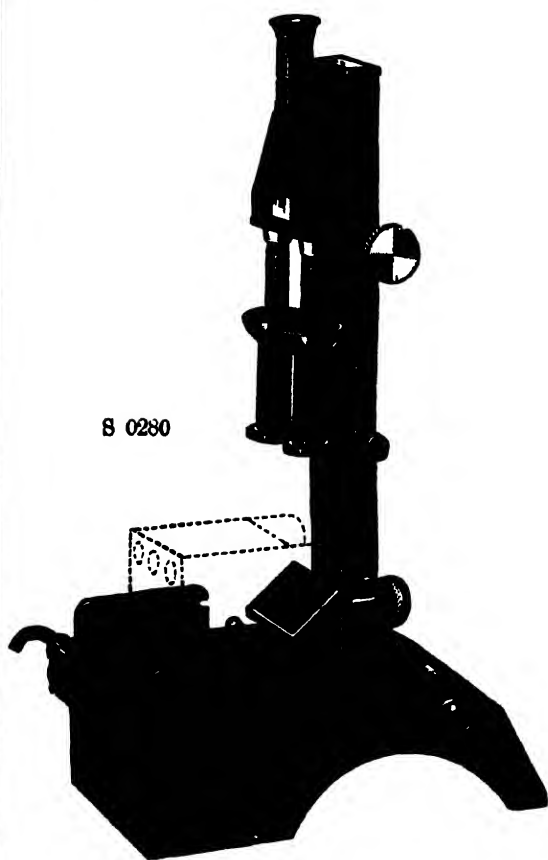
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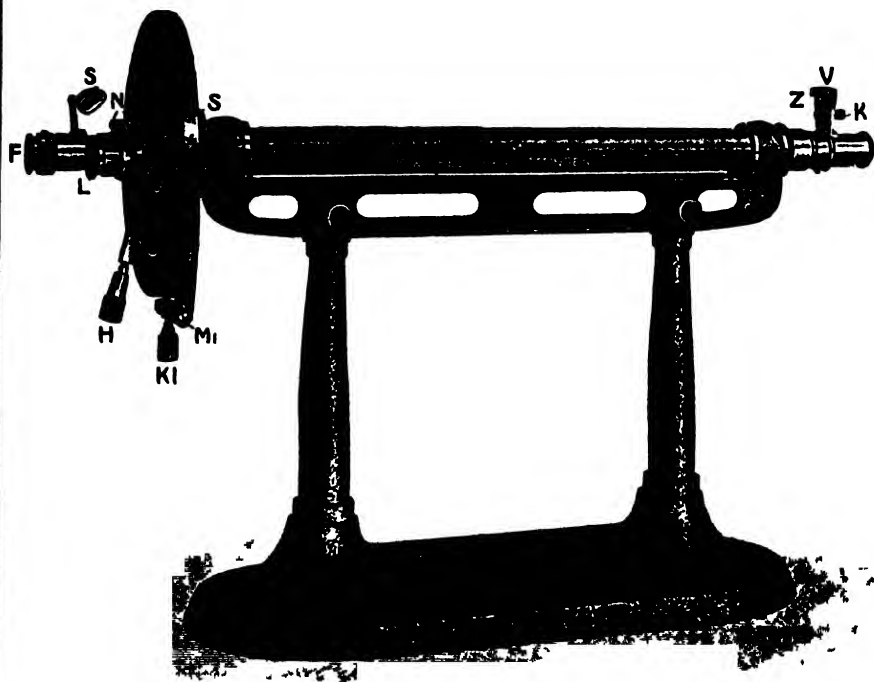
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# **Studies in the Kinetics of the Coagulation of Colloids.**

## **Part V. The Variation of Viscosity during Coagulation.**

BY SHRIDHAR SARVOTTAM JOSHI AND K. S. VISWANATH.

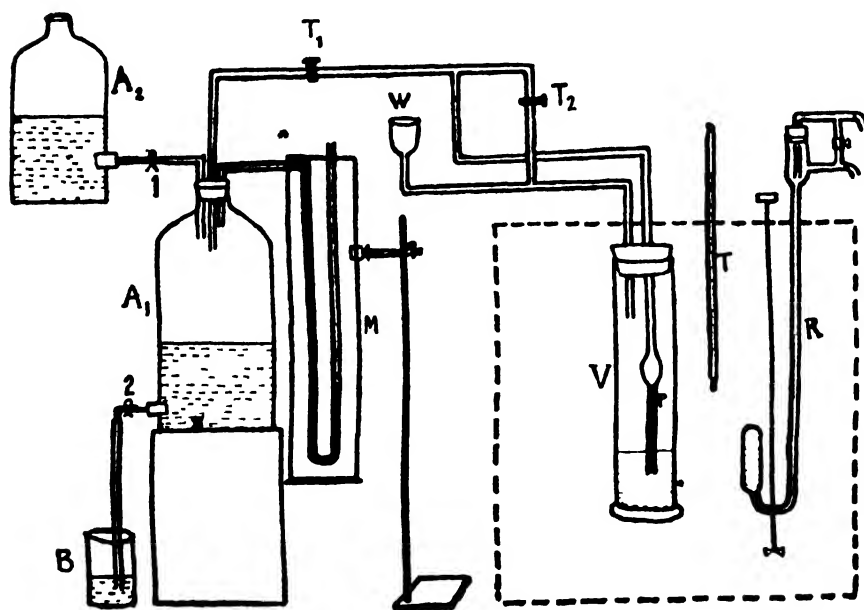
The work of Miyazawa (*J. Chem. Soc.*, Japan, 1912, **33**, 1179), Freundlich and Ishizaka (*Trans. Faraday Soc.*, 1913, **9**, 66), Wo. Ostwald (*ibid* , p 34), Pauli (*ibid* , p 64), Gann (*Koll. Chem. Beih.*, 1916, **8**, 65), Smoluchowski (*Kolloid Z* , 1916, **18**, 190), and numerous other workers, has shown the marked utility of viscometric observations in the kinetic studies of coagulations. The interesting work, especially of Freundlich (*loc. cit.*, *cf.* also Freundlich, "Colloid and Capillary Chemistry. Eng. Trans., 1926) and of Gann (*loc. cit.*), has been the chief and earliest evidence for *autocatalysis* in the coagulation of colloids. Evidence was, however, adduced in the previous papers in this series (*J. Indian Chem. Soc.* 1931, **8**, 11, 337; 1932, **9**, 157, and especially the *P. C. Ray Commemoration Volume of Indian Chem. Soc.*, pp 41-52) to show that though prevalent under certain conditions, *autocatalysis* can not be considered as a general characteristic of the coagulation phenomenon. It is also of interest to observe that practically all the systematic work on the viscometric examination of the kinetics of coagulation is restricted to lyophilic sols. The following work was, therefore, undertaken to extend the above line of work to lyophobic, and especially to examine what support can be given to the view mentioned above regarding the nature of the coagulation process. This has been studied here in the case of arsenious sulphide and gelatine and their mixtures when coagulated by differently concentrated solutions of potassium chloride.

### **EXPERIMENTAL**

A review of the literature shows that practically all the previous work on the viscometric examination of the kinetics of coagulation

was carried out by the use of the Ostwald's viscometer. This requires a knowledge of the transpiration time of the liquid and the corresponding density. Now the measurement of the last quantity is rather inconvenient in the case of a coagulating sol. Unfortunately, this determination is absent in the majority of papers on the viscosity changes of coagulating sols, which detracts at any rate from the precision of the interpretation of the viscosity term applied to such data. A convenient method in such cases is the one due to Scarpa (*Gazzetta*, 1910, **40**, 271; *cf.* also Farrow, *J.Chem. Soc.*, 1912, **101**, 347); this does not necessitate a knowledge of the density of the liquid. This method was, therefore, adopted with modifications, described in the sequel, which add appreciably to the precision of

FIG. A.



measurement. A suitable quantity of water from the aspirator  $A_1$  was let out in B (Fig. A). The pressure diminution thus produced is observed on the manometer M, and communicated to the pipette P by opening the tap  $T_1$ ,  $T_2$  being closed.  $t_1$ , the time for the liquid to rise between two marks made on P under this suction was noted.  $T_1$  is then closed and  $T_2$  opened. This connects P with the atmosphere through a quantity of glass wool, kept at W in order to avoid dust, etc.,



from entering the apparatus; the liquid in P therefore begins to fall. This time  $t_2$  similar to  $t_1$  is noted,  $\eta$  the viscosity is then given by

$$\eta = K \cdot \frac{t_1 \cdot t_2}{t_1 + t_2}$$

where  $K$ , a constant, is determined from a knowledge of  $t_1$  and  $t_2$  for a liquid like water for which  $\eta$  (0.7225 centipoise at 35°) is known. The aspirator  $A_1$  connected with  $A_2$  is rather convenient in order to replenish water in the latter. The use of stop-cocks  $T_1$  and  $T_2$  well lubricated with good vacuum grease, instead of pinch cocks, added greatly to the reproducibility of results, and specially to an accurate adjustment of the pressure in  $A_1$ , prior to the observation of  $t_1$ . This precaution appears to have been neglected by previous workers.

Majority of the experiments were made with the arsenious sulphide sol. It was prepared, and its colloid content determined, as described in Part I (*J. Indian Chem. Soc.*, 1931, 8, 11). The last quantity in all the experiments (except those to which Fig. 5 refers) was 4.5 g. of  $As_2S_3$  per litre in the coagulating mixture. Coagulations were also studied where the above colloid was protected by different concentrations of gelatine solutions. These were prepared by soaking in distilled water weighed pieces of gelatine cut from pure sheet. 20 C.c. of the colloid and 10 c.c. of one of the gelatine solutions were mixed and allowed to stand for 15 minutes. To the mixture was then added 10 c.c. from variously concentrated solutions of potassium chloride and the viscosity determined at successive intervals during the progress of coagulation. These results have been shown graphically in Figs 3 and 4 (*cf.* also Tables III and IV). Figs. 1, 2 and 5 (also Tables I, II and V) refer respectively to viscosity variations when only the arsenious sulphide sol, and gelatine solutions were mixed with solutions of potassium chloride. The temperature of the thermostat was maintained at 35° in all the experiments. Stirring was discontinued during observations of  $t_1$  and  $t_2$ . Concentrations of the electrolyte added were such as to have the coagulation prolonged over a fairly wide time period. Observations of viscosity were discontinued as soon as flocculation (that is, the formation of just visible heterogeneities consisting of coagulated particles tending to deposit a fine film on the inside of the pipette P in Fig. A) sets in. During the course of this work it was observed that immediately after the

start of the coagulation, the viscosity—coagulation time curve almost always showed a minimum. Since this phenomenon does not appear to have been studied previously, it has been investigated here in some detail. The data given in Tables I—IV were read off the corresponding curves in Figs. 1—5. Fig. 6 relates the coagulator concentration with the time interval up to the attainment of the first minimum mentioned above from the start of coagulation.

TABLE I (cf Fig. 1).

Colloid used =  $As_2S_3$ 

Reference.	KCl conc.	Initial viscosity.	First minimum viscosity.	Time corresponding to $\eta_m$ in mins.	Viscosity diminution in per cent.	Final observed viscosity.	Time corresponding to $\eta_f$ in mins.	Remarks
Curve No.		$\eta_i$	$\eta_m$			$\eta_f$		
1	N/16	0.714	0.732	13	1.6	1.27	130	Flocculation commenced after this
2	N/16.6	0.714	0.732	11	1.6	0.98	136	Do
3	N/17.4	0.737	0.727	11	1.4	1.60	185	

TABLE II (cf Fig. 2).

Colloid used =  $As_2S_3$ .

4	N/17.7	0.743	0.729	19	1.9	0.752	180	No flocculation ; $\eta_f$ after 24 hrs. 0.789
5	N/18.2	0.788	0.727	27	1.5	0.805	225	No flocculation ; $\eta_f$ after 24 hrs. 0.839
6	N/19	0.737	0.723	28	1.8	0.731	218	No flocculation ; $\eta_f$ after 24 hrs. 0.752
7	N/20	0.737	0.732	25	0.7	0.742	245	No flocculation ; $\eta_f$ after 24 hrs. 0.859

TABLE III.

Colloid used =  $\text{As}_2\text{S}_3$  protected by 0.125% gelatine.

Reference.	KCl conc.	Initial viscosity.	First minimum viscosity.	Time corresponding to $\eta_m$ .	Viscosity diminution in per cent.	Final observed viscosity.	Time corresponding to $\eta_f$ .	Remarks.
Curve No.		$\eta_i$	$\eta_m$			$\eta_f$		
8	N/10	0.748	—	—	0.638	41		Flocculation just perceptible after about 50 mins.
9	N/11.1	0.750	0.739	10	1.5	0.875	100	No flocculation ; after 20 hrs. 1.11
10	N/11.4	0.746	0.738	11	1.1	1.28	230	Flocculation just perceptible after 23 hrs. after 23 hrs. 2.58
11	N/11.7	0.745	0.739	10	0.8	1.19	300	No flocculation
12	N/12.5	0.743	0.738	11	0.7	0.758	166	Do
13	N/13.3	0.785	0.770	11	0.8	0.958	180	Do

TABLE IV (cf. Fig. 4).

Colloid used =  $\text{As}_2\text{S}_3$  protected by 0.05% gelatine.

14	N/10	0.779	0.766	11	1.7	0.767	125	No Flocculation. $\eta$ rises to 0.847 after 24 hours
15	N/13.3	0.755	0.741	12	1.9	0.743	251	No flocculation ; $\eta$ becomes practically constant

TABLE V.

16	N	0.754	0.749	12	0.7	0.748	—	$\eta$ fluctuates about
17	N/2	0.751	0.749	12	1.2	—	—	a mean value after initial fall
18	N/2	0.738	0.729	25	1.2	—	—	Do

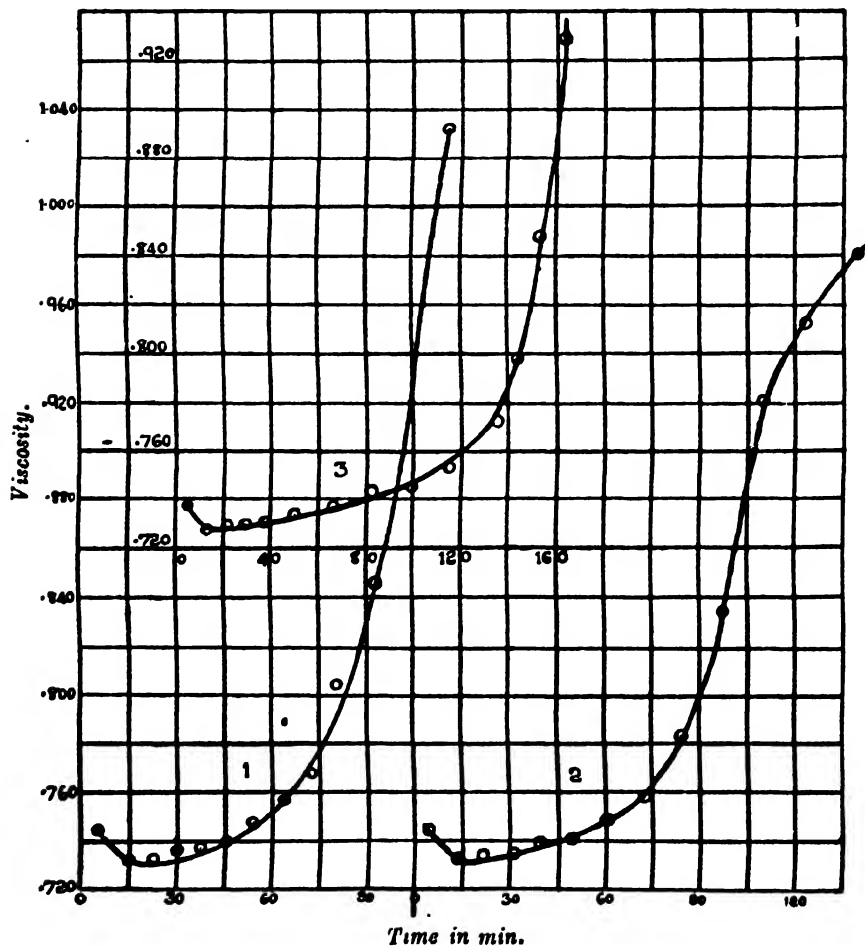
No. 16 and 17 refer to  $\text{As}_2\text{S}_3$  sol protected by 0.1% gelatine and No. 18 by 0.05% gelatine.

## DISCUSSION.

These results show that the rise of viscosity during the period observed diminishes rapidly, *e.g.*, from about 70% in 130 minutes to about 1% in over 200 minutes, as the concentration of the co-

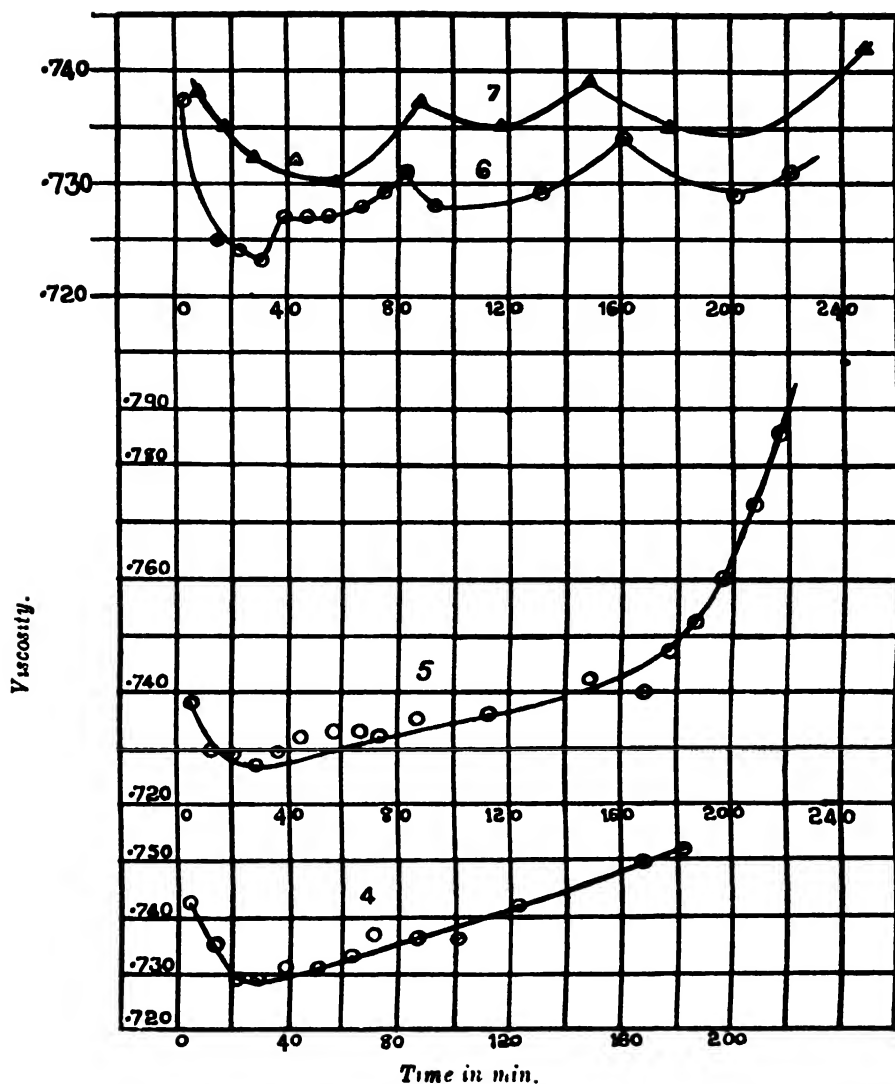
gulator is reduced from  $N/16$  to  $N/20$  (cf. Tables I, II; curves 1, 7, Figs. 1 and 2). This result is in agreement with the known profound influence of changes in the concentration of the coagulator upon the rate of coagulation in the region of the *slow coagulation*. Although sufficiently numerous and strictly comparable data are not available it would appear that lyophilic sols do not show so great a sensitivity to changes in the concentration of the coagulator. This deduction is supported by the results of Freundlich and Ishizaka (*loc. cit.*) for the coagulation of such a typical lyophilic sol as aluminium hydroxide produced by potassium salicylate solutions in the range, 5 to  $\frac{1}{10}$  millimols per litre, and also those obtained in this work (cf. Tables III, IV).

FIG. 1.



The coagulator conc. for curves 1, 2, 3 were  $N/16$ ,  $N/16.6$ ,  $N/17.4\text{-KCl}$  respectively.

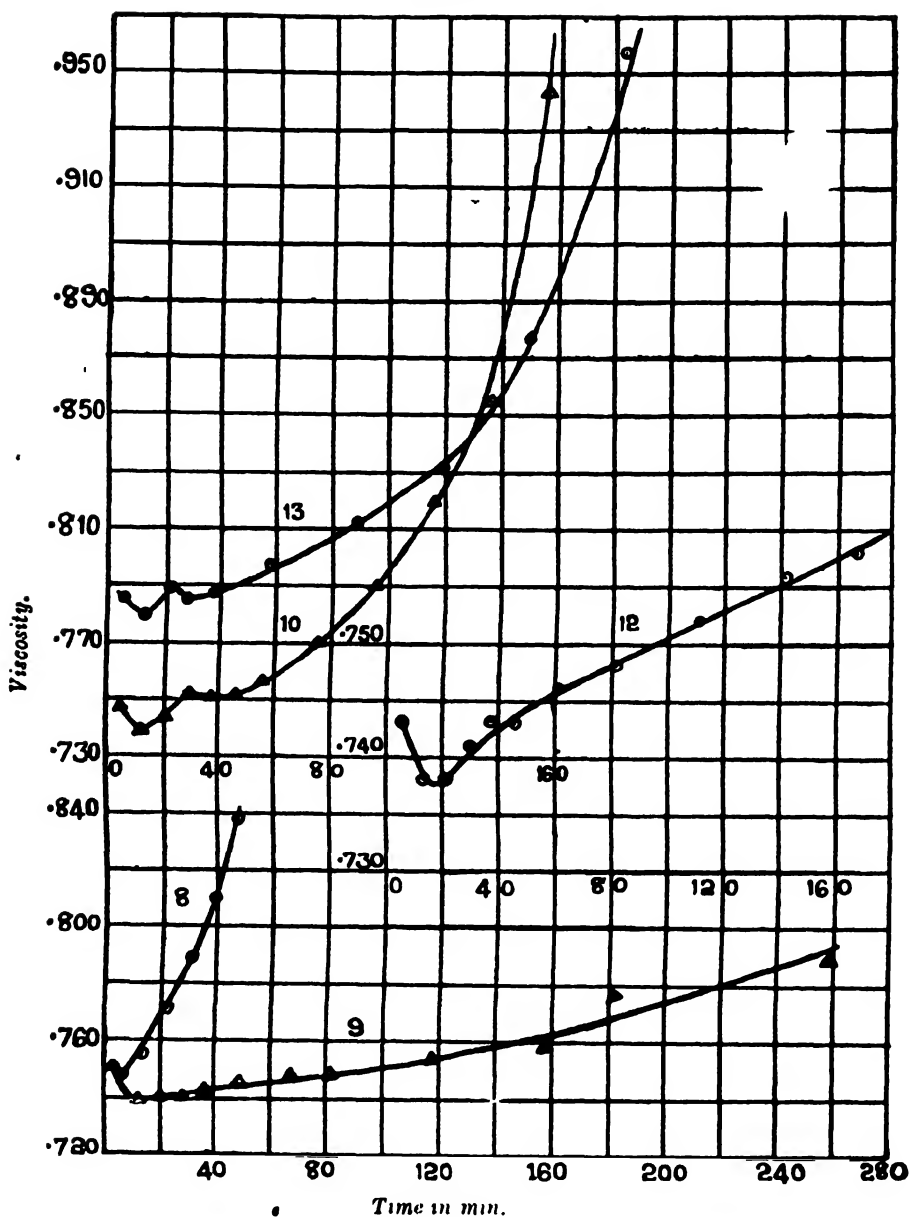
FIG. 2.



The coagulator conc. for curves 1, 5, 6 and 7 were  $N/17.7$ ,  $N/18.2$ ,  $N/19$  and  $N/20$ -KCl respectively.

It is interesting to note from curves 1—5 in Figs. 1 and 2 that soon after a small initial fall, the viscosity increases markedly after an appreciable period of a comparatively marked low rate of changes. Assuming tentatively that in the main, viscosity and coagulation change together and in the same sense, this might be ascribed to *autocatalysis* which ordinarily is the acceleration of the rate of a chemical reaction by the accumulation of the products of the reaction. Its mechanism in the present type of changes is generally considered to be the coagulum particles serving as nuclei for further coagulation. These

FIG. 3.

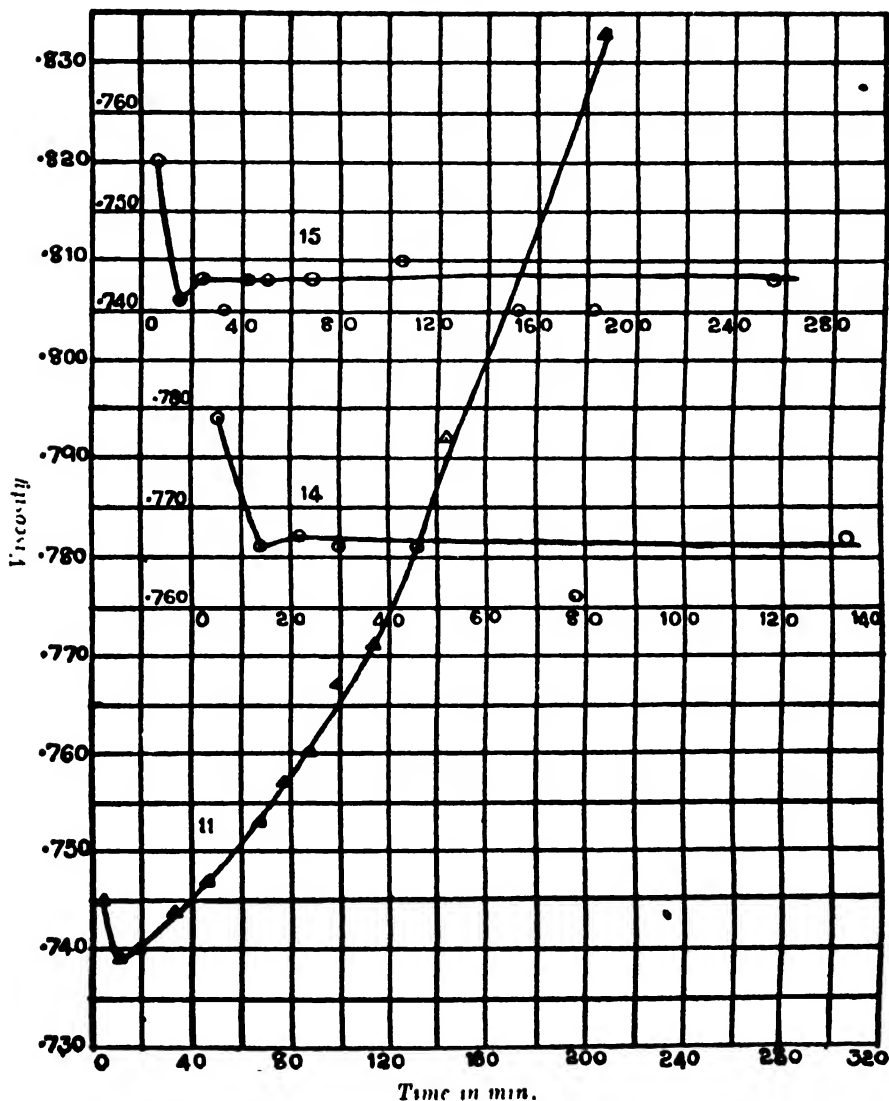


The colloid was protected by 0.025% gelatine sol. The coagulator conc. for curves 8, 9, 10, 12 and 13 were  $N/10$ ,  $N/11.1$ ,  $N/11.4$ ,  $N/12.5$  and  $N/13.3$   $KCl$  respectively.

curves also show that the period after which the coagulation rate becomes large, tends to increase as the concentration of the coagulator is diminished. At still higher dilutions (*cf.* curve 4, and also curves 6, 7, Fig. 2) the above period would appear to cover practically the entire time of observation; the final value of viscosity in these

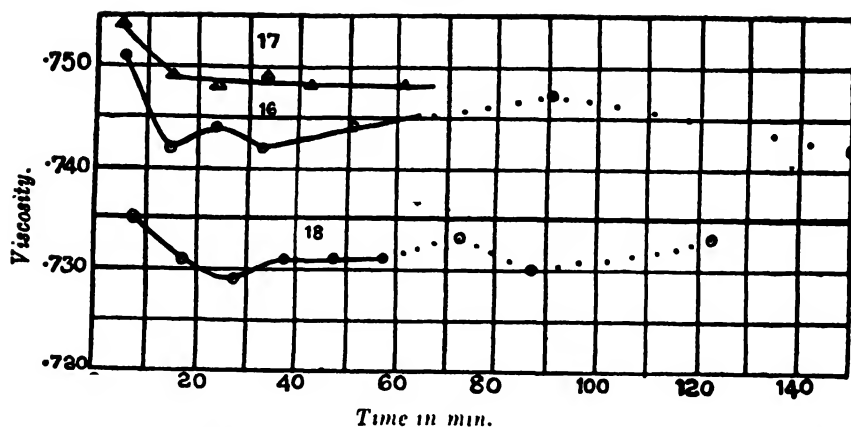
coagulations is but slightly higher than the initial one. This slow rising section of the curve is not so conspicuous in most of the coagulation—time curves in Figs. 3 and 4 which show the influence of different proportions of gelatine in the coagulating mixture. This might be ascribed either to the higher concentration of the coagulator used, or to the presence of the protector, or what is more probable, to both these factors.

FIG. 4.



The colloid was protected by 0.025% (curve 11) and 0.059% gelatine (curve 14—15). The coagulator conc. for curves 11, 14 and 15 were  $N/11.7$ ,  $N/13.3$  and  $N/10$ -KCl respectively.

FIG. 5.



Coagulation of gelatine solution, 0.1% for curves 16 and 17 and 0.05% for curve 18. Coagulator conc. for curves 16–18 were  $N/2$ ,  $N$  and  $N/2$ -KCl respectively.

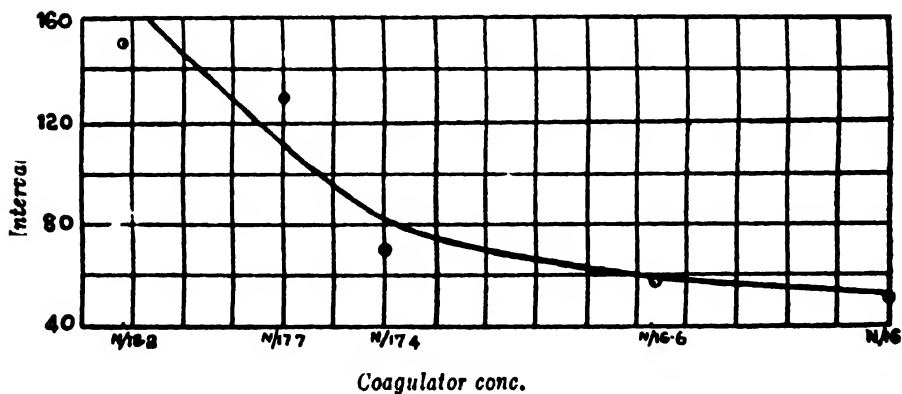
Two features of some interest are noticeable from curves in Figs. 1–5. The first is the almost invariable initial diminution of viscosity and second, the fact that in practically no case does the viscosity rise smoothly during the progress of coagulation. Both these facts militate against the use of viscosity as a quantitative measure of coagulation at any rate with low concentrations of the coagulator. Accuracy of the experimental arrangement used here, and the number of observations taken indicate that the non-uniformities and breaks on these curves can not be ascribed to experimental error. In our opinion, these suggest that coagulation, especially in the *slow region*, is a complex process in which the particles undergo a succession of changes, presumably both as to their size and nature. This would appear to be the main reason for the breakdown of the Smoluchowski's theory (*Z. physikal. Chem.*, 1917, 92, 129), or its simple extension based on the assumption that coagulation is but a continued coalescence of particles discharged initially completely, or partially.

It is probable, for instance, starting with a certain number of primaries mixed with the electrolyte, the formation of agglomerates through successive coalescence might prevail as the main process producing the viscosity change in a certain sense during the given period. Now, after this period the agglomerates might suffer a breakdown due (i) to instability induced as a result of the attainment of a certain size and structure during the coalescence, or (ii) by the action of similarly charged ions. This will produce a viscosity change in a direction opposite to what happened just previously.



Observed over a prolonged time, the operation of the two sets of factors mentioned above will produce mainly fluctuations on the coagulation—time curve. Evidence was cited in a previous paper (Joshi and Joga Rao, *J. Indian Chem. Soc.*, 1933, 10, 273) that viscosity is particularly susceptible to even such alterations in a colloid as might be missed for example by the familiar turbidity method of observing coagulation. In coagulations due to higher concentrations of the coagulator, velocity of the change is so great that the coalescence process passing through the formation of agglomerates ends only with precipitation which ordinarily is an irreversible process. It follows, therefore, that fluctuations in the sense described above are to be anticipated only when dilute solutions of the coagulator are employed. A comparison of curves 6, 7 in Fig. 2, curves 14, 15 in Fig. 4, and 16, 17, 18 in Fig. 5 with the rest illustrates clearly the above possibility. It might be observed incidentally that the above suggestion, regarding the nature of possible conditions under which there is no net advance in the coagulation, might also explain results in connection with the 'Bodländer's limit.'

FIG. 6.



The initial diminution of viscosity observed in practically all the coagulations varies in the range from 0.7 to 1.0% of the initial viscosity of the colloid (*cf.* Tables I—V). It is interesting to note that the time reckoned from the start of coagulation up to the occurrence of this fall of viscosity is roughly constant for a given series of coagulations. It is also of interest to note from Fig. 6 that the interval during which viscosity remains at, or below the first minimum, rises rapidly with the dilution of the coagulator, and would

tend to be infinitely large for very low dilutions, presumably corresponding to the 'Bodländer's limit' for the colloid used. This initial diminution must be regarded as distinctive of at least one of the stages constituting the progress of coagulation at any rate in the *slow region*. Whilst it has not been possible so far to obtain a complete elucidation of this phenomenon, it is important to mention that this initial fall of viscosity, and the occurrence of fluctuations, (the latter under conditions mentioned in the above discussion, the coagulation being measured by different means) have been found to be features of almost universal occurrence in diverse coagulating systems in *slow region*. A discussion of these results is reserved for a later communication.

#### SUMMARY.

*Slow* coagulations of simple arsenious sulphide sols and when protected by different amounts of gelatine, as well as of pure gelatine sols of different strengths, due to potassium chloride solutions in the range  $N$  to  $N/20$  have been examined by measuring the viscosity of the coagulating system. The coagulation—time curves show some or all of the following three characteristics: (i) The viscosity shows an initial diminution (up to a maximum of about 1.9%), the corresponding time being roughly constant in a given series of coagulations. (ii) The next section of the curve rises slowly at first and then rapidly, indicative of *autocatalysis*. (iii) The last feature is absent for high as well as for very low concentrations of the coagulator. Under the last factor, subsequent to (i) the coagulation—time curves show only periodic fluctuations without an appreciable net increase of viscosity, for which an explanation has been suggested.

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# Experiments on the Synthesis of Santenone. Part I.

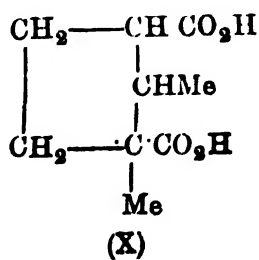
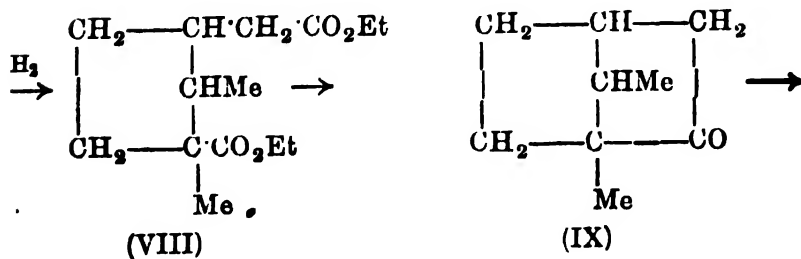
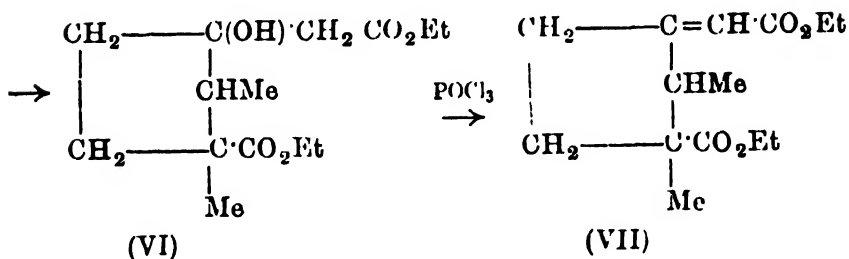
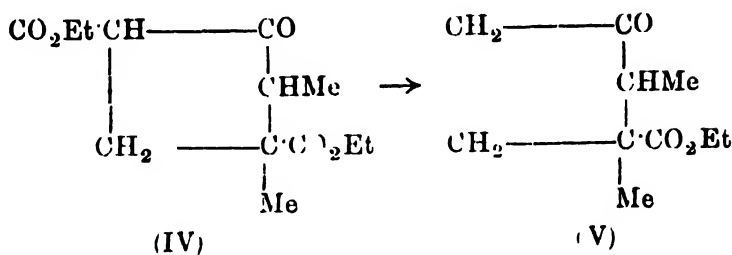
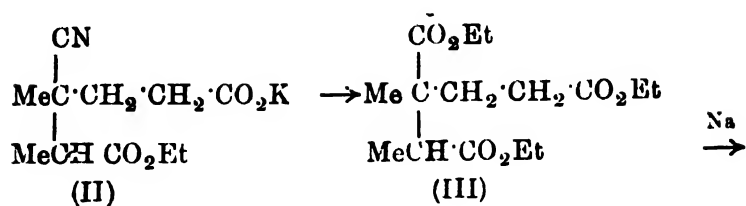
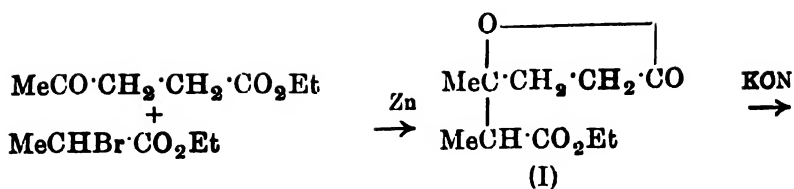
## A Synthesis of Homosantenic Acid.

BY SURESH CHANDRA SEN-GUPTA.

1-Santenone (IX) occurs in Indian sandalwood oil (*Schimmel's Report*, 1910, Oct, p. 98) and the inactive form has been prepared by Semmler and Bartell (*Ber.*, 1907, **40**, 4467) by the oxidation of  $\pi$ -norborneol with chromic acid and also by Aschan (*Ofvers. Finska Vet. Soc.*, 1910, **53** A, No 8, p.17) by the oxidation of sentene with potassium dichromate-sulphuric acid mixture. the latter reaction involving a Wagner rearrangement.

The constitution of santenone has been established by its oxidation to santenic acid (X) recently synthesised by Komppa (*Ber.*, 1932 **65**, 1710). No work on the synthesis of santenone has as yet been attempted. The present investigation has been undertaken with a view to synthesise the ketone and this has been attempted following Ruzicka's synthesis of fenchone (*Ber.*, 1917, **50**, 1362).

Ethyl levulinate and ethyl  $\alpha$ -bromopropionate were condensed by Reformatsky's reaction giving the lactone of ethyl  $\beta$ -hydroxy  $\gamma$ -dimethyl adipate (I), which was converted into the cyano-ester (II) by means of potassium cyanide and the latter on hydrolysis and esterification by the alcohol vapour method gave ethyl  $\alpha\beta$ -dimethylbutane- $\alpha\beta\delta$ -tricarboxylate (III). This tricarboxylic ester by the application of Dieckmann reaction with molecular sodium was converted into ethyl 2:3-dimethylcyclopentanone-8:5-dicarboxylate (IV), the latter on hydrolysis gave 2:3-dimethylcyclopentanone-3-carboxylic acid; the ethyl ester (V) of this keto acid condensed with bromoacetic ester in presence of zinc giving the hydroxy ester (VI). This on dehydration with phosphorus oxychloride gave the unsaturated dehydrohomosantenic ester (VII) which on reduction and hydrolysis yielded homosantenic acid. Work is in progress on the synthesis of santenone by the distillation of the lead salt of homosantenic acid.



## EXPERIMENTAL.

*Lactone of ethyl  $\beta$ -hydroxy- $\alpha\beta$ -dimethyladipate* (I).—Ethyl levulinate (108 g.), ethyl  $\alpha$ -bromopropionate (137 g.) and zinc wool (50 g.), diluted with dry benzene (250 c.c.) were heated on the water-bath till the exothermic reaction commenced. When the brisk action subsided, the reaction was finally completed by heating on the water-bath for 1 hour; the product was decomposed with ice-cold dilute sulphuric acid, the benzene layer separated, washed with caustic soda solution and water, dried with calcium chloride, benzene removed, when the lactonic ester distilled as a thin colourless oil, b.p.  $148-49^{\circ}/8$  mm., yield 90 g. (Found: C, 59.7; H, 8.1.  $C_{10}H_{16}O_4$  requires C, 60.0; H, 8.0 per cent).

*Ethyl  $\alpha\beta$ -dimethylbutane- $\alpha\beta\delta$ -tricarboxylate* (III).—The lactonic ester (90 g.) and finely powdered potassium cyanide (43 g.) were heated under reflux for 10 hours at  $200-20^{\circ}$ . The brown reaction product was hydrolysed by heating with 250 c.c. of concentrated hydrochloric acid for 10 hours. The solution was evaporated on the water-bath almost to dryness, the residue thoroughly extracted with ether, dried, ether removed. Through a hot solution of the residue in absolute alcohol (200 c.c.) and concentrated sulphuric acid (25 c.c.) was passed alcoholic vapour from 2 litres of alcohol. The alcohol was distilled off, the solution diluted with water, extracted with ether, dried, ether removed and distilled. Repeated fractionation of the portion collected at  $130-160^{\circ}/5$  mm. gave 40 g. of the ester at  $147-52^{\circ}/5$  mm. It is a light-coloured thin liquid (Found: C, 59.3; H, 8.7.  $C_{15}H_{26}O_6$  requires C, 59.6; H, 8.6 per cent).

*Ethyl 2:3-dimethylcyclopentanone-3:5-dicarboxylate* (IV) was prepared by heating the tricarboxylic ester (35.5 g.) with molecular sodium (3.5 g.) in dry benzene (150 c.c.) for 1 hour on the water-bath, whereby the sodium quickly dissolved. The light-coloured clear liquid was cooled, decomposed with ice, shaken with dilute sulphuric acid and the benzene extract washed, dried, benzene completely removed and distilled, when it collected at  $145-50^{\circ}/5$  mm. It gave strong ferric chloride coloration, yield 20 g. (Found: C, 61.0; H, 7.9.  $C_{13}H_{20}O_5$  requires C, 60.9; H, 7.8 per cent).

2:3-Dimethylcyclopentanone-3-carboxylic acid was prepared by heating the foregoing keto-dicarboxylic ester (20 g.) with concentrated hydrochloric acid (85 c.c.) and water (100 c.c.) for 5 hours.

The clear aqueous solution was saturated with ammonium sulphate and repeatedly extracted with ether, the ethereal solution dried and the solvent removed. On distillation a small fraction (2 g.), b.p. 100-150°/5 mm. evidently consisting of the ester, was obtained along with a large fraction (11 g. of the pure acid) of a colourless thick liquid, b.p. 150-53°/5 mm. (Found: C, 61·3; H, 7·8.  $C_8H_{12}O_3$  requires C, 61·5; H, 7·7 per cent).

The *semicarbazone* was prepared in aqueous solution and crystallised from water or dilute alcohol, m.p. 208°. (Found: C, 50·4; H, 6·9.  $C_9H_{15}O_3N_3$  requires C, 50·7; H, 7·0 per cent).

The *ethyl ester* (V).—The acid (10 g.) was heated for 14 hours with a solution of sodium (1·8 g.) in absolute alcohol and ethyl iodide (13 g.). Alcohol was distilled off, the residue diluted with water and repeatedly extracted with ether, dried, ether removed, when the ester distilled almost completely at 105-106°/5 mm. as a colourless mobile oil, yield 9 g. (Found: C, 65·1; H, 8·7.  $C_{10}H_{16}O_3$  requires C, 65·2; H, 8·7 per cent).

The *semicarbazone* crystallised from methyl alcohol in colourless prismatic needles, m.p. 191°. (Found: C, 54·4; H, 7·9.  $C_{11}H_{19}O_3N_3$  requires C, 54·8; H, 7·9 per cent).

*Ethyl dehydrohomosantenate* (VII).—Ethyl dimethylcyclopentanonecarboxylate (12 g.), ethyl bromoacetate (12 g.) and zinc wool (6 g.) diluted with benzene (50 c.c.) were heated on the water-bath with the addition of a crystal of iodine until the vigorous reaction set in. It was finally heated on the water-bath for 1 hour to complete the reaction. After treating with ice-cold dilute sulphuric acid, the benzene layer was washed with caustic soda solution, dried and distilled, when the unchanged keto-ester (1·6 g.) collected at 100-20°/4 mm. and a colourless oil (8·4 g.) at 125-50°/4 mm. consisting of the oxy- and the dehydro-ester. This was completely converted into the unsaturated ester by heating on the water-bath with phosphorus oxychloride (3 g.) in dry benzene (40 c.c.) for 3 hours. This benzene solution was successively treated with cold water and dilute caustic soda, dried and distilled, when 6·5 g. of a pleasant smelling liquid collected at 125-30°/4 mm. It decolourised bromine water readily. (Found: C, 65·6; H, 8·6.  $C_{14}H_{22}O_4$  requires C, 66·1; H, 8·7 per cent).

*Homosantenic ester* (VIII).—The dehydro-ester (5 g.) dissolved in absolute ether (25 c.c.) was reduced with hydrogen in presence of platinum oxide catalyst (3 g.) under atmospheric pressure. It.

absorbed the calculated amount of hydrogen in about 2 hours and boiled at  $130-35^{\circ}/5$  mm. (Found: C, 65.4; H, 9.5.  $C_{14}H_{24}O_4$  requires C, 65.6; H, 9.4 per cent).

*Homosantenic acid*.—The free acid was obtained by hydrolysing the ester with alcoholic potash, evaporating off the solvent, and the residue, dissolved in a small amount of water, was acidified with hydrochloric acid, when the homosantenic acid immediately separated out. On repeated crystallisation from water it was obtained as almost colourless needles, m.p.  $170^{\circ}$ . (Found. C, 60.3; H, 7.9.  $C_{10}H_{16}O_4$  requires C, 60.0; H, 8.0 per cent).

The author desires to express his thanks to Dr. P. Neogi and to Dr. M. Q. Khuda for the kind facilities they have given for carrying on this work and to Dr. J. C. Bardhan for his helpful interest in this investigation.

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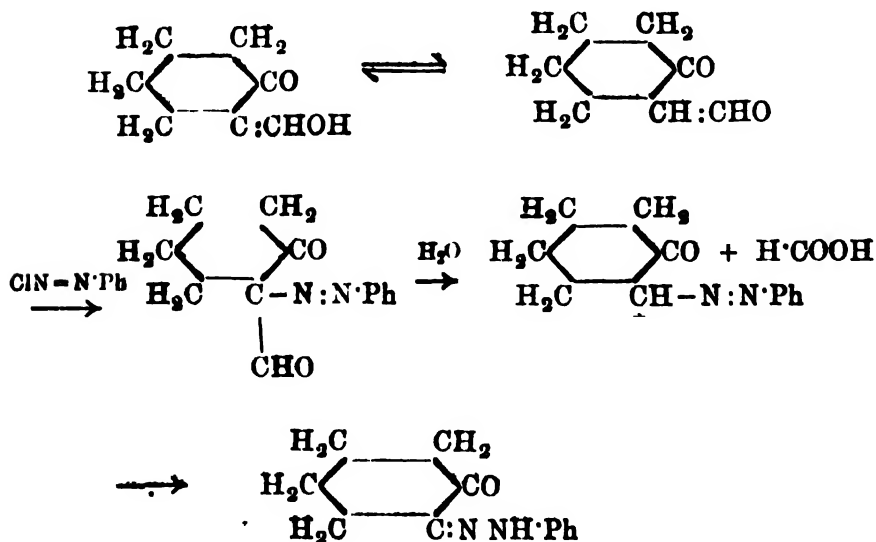




## Reaction of Diazonium Salts with Open-chain Hydroxymethyleneketones.

BY SACHINDRA NATH ROY AND HEMENDRA KUMAR SEN.

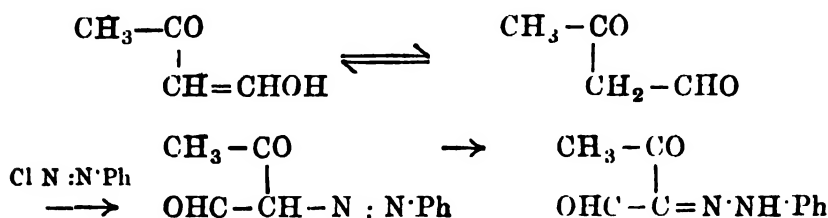
It was observed by one of us (*J. Indian Chem. Soc.*, 1927, **4**, 477) that diazobenzene chloride reacts with cyclic hydroxymethyleneketones in the aldehydic phase of the latter. This was established by the fact that when diazonium chloride reacts with hydroxymethylenecyclohexanone in the presence of sodium acetate, the reaction product obtained is identical with the monophenylhydrazone of diketohexamethylene. It is evident that the formation of a monophenylhydrazone in such cases must of necessity be attended with the removal of the formyl group to give the required hydrogen for the formation of a phenylhydrazone. The reaction was accordingly represented as below :



The labile hydrogen atom which was attached to the carbon atom (\*) thus migrates to a nitrogen atom, attended with a shift of double bond, causing the formation of a hydrazone. The azo derivative is,

therefore, not realised. As all these transformations are best explained by assuming the aldehyde phase, hydroxymethylenecyclohexanone need not be considered as a permanently enolised  $\beta$ -diketone.

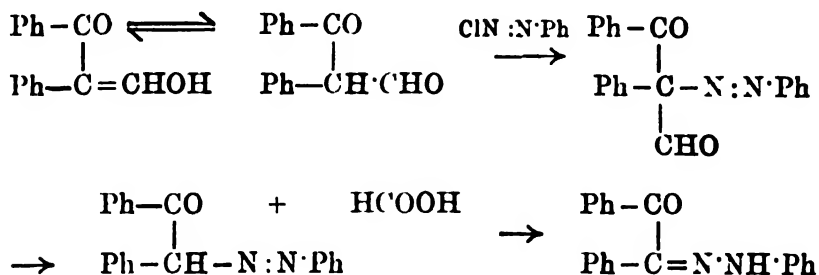
Benary, Meyer and Charisius (*Ber.*, 1926, 59, 109) on the other hand, have shown that open-chain hydroxymethyleneketones react with diazobenzene chloride giving the following type of compounds, in which the formyl group remains unaffected, although the hydrazone is the final product.



To explain the elimination of the formyl group (a fact which was proved by analysis and the detection of ethyl formate in the reaction mixture) in the case of cyclic hydroxymethyleneketones as distinct from the open-chain hydroxymethylene compounds described by these authors, it was advanced by one of us that in the open-chain hydroxymethyleneketones used by Benary and his collaborators, there is a hydrogen atom in the ketone, available for the formation of phenylhydrazone, whilst in cyclic hydroxymethyleneketones, no such labile hydrogen atom is present. Hence, if the tendency to form a hydrazone is great, formyl group will have to be eliminated to supply the necessary hydrogen for the transformation of the azo derivative to hydrazone.

The present work was undertaken in order to investigate whether it was a characteristic property of open-chain hydroxymethyleneketones to retain the formyl group, while reacting with diazonium chloride, or whether the above hypothesis holds good in all cases of reaction between diazonium chloride and hydroxymethyleneketones, cyclic or open-chain, where there was no extra hydrogen available for the formation of phenylhydrazone. With this end in view, the reaction between hydroxymethylenedesoxybenzoin (prepared by the action of ethyl formate and sodium ethoxide on desoxybenzoin in dry ethereal solution) and diazobenzene chloride was studied. According to our hypothesis, hydroxymethylenedesoxybenzoin, which is an open-chain hydroxymethyleneketone, containing no available hydrogen atom unlike Benary's compounds for the

formation of phenylhydrazone, must have its formyl group split off in the following way to give rise to monophenylhydrazone of benzil :



That the reaction product was monophenylhydrazone of benzil was proved by analysis as well as by the following facts :

(i) It was found to be identical with the monophenylhydrazone of benzil prepared by Bülow (*Annalen*, 1885, **236**, 194) by warming equimolecular quantities of benzil and phenylhydrazine.

(ii) The diphenylhydrazone obtained by heating benzil and excess of phenylhydrazine was identical with the product obtained by heating our reaction product with phenylhydrazine.

The action of diazonium chloride or substituted diazonium chlorides on open-chain hydroxymethyleneketones having no available hydrogen atom for the specific reaction mentioned above, invariably gave rise to monophenylhydrazones or substituted monophenylhydrazones in the same way as in the case of cyclic hydroxymethyleneketones.

#### EXPERIMENTAL.

*Condensation of hydroxymethylenedesoxybenzoin and diazobenzene chloride: Formation of monophenylhydrazone of benzil.*—Diazotised aniline (1 mol.) was added to a solution of hydroxymethylenedesoxybenzoin (1 mol.) in aqueous alcohol containing excess of sodium acetate, cooled below 0°. A yellowish sticky mass separated which was filtered, washed with water, dried and crystallised when yellowish brown needles from dilute acetic acid were obtained, m.p. 128-29°. When crystallised from dilute alcohol, the colour becomes light yellow. It is insoluble in alkali. (Found: N, 9.5, Calc.: N, 9.84 per cent).

The filtrate was distilled on a water-bath and in the distillate, collected between 60° and 80°, a strong smell of ethyl

formate was noticed. The distillate gave a white precipitate of mercurous chloride with a solution of mercuric chloride.

The benzilmonophenylhydrazone, thus obtained, was heated with an equimolecular quantity of phenylhydrazine in the presence of a little glacial acetic acid on a water-bath for  $\frac{1}{2}$  hour. The bright yellow precipitate obtained on dilution was filtered and washed with alcohol. It crystallised from hot acetic acid as bright yellow needles, m.p.  $225^{\circ}$ . It was found to be identical with benzil-diphenylhydrazone, prepared otherwise. (Found: N, 14.72. Calc.: N, 14.35 per cent).

*Condensation of hydroxymethylenedesoxybenzoin and diazo-p-nitrobenzene chloride: Formation of benzilmono-p-nitrophenylhydrazone.*—The condensation was effected in the usual way and the product crystallised from dilute alcohol as yellowish orange needles, shrinking at  $176^{\circ}$  and melting at  $180^{\circ}$ . It is soluble in acetic acid and alcohol and is identical with benzilmono-p-nitrophenylhydrazone, prepared in other ways. (Found: N, 12.09. Calc.: N, 12.23 per cent).

*Benzildi-p-nitrophenylhydrazone.*—By heating the above mono-p-nitrophenylhydrazone with an equimolecular quantity of p-nitrophenylhydrazine in glacial acetic acid solution for  $\frac{1}{2}$  hour on the water-bath, the di-p-nitrophenylhydrazone was prepared. On cooling and dilution with water, a reddish mass was obtained which is sparingly soluble in alcohol. This was filtered, washed and crystallised from acetic acid when deep red needles were obtained melting at  $290^{\circ}$ , identical with di-p-nitrophenylhydrazone prepared otherwise. (Found: N, 17.8. Calc.: N, 17.5 per cent).

*Benzil-p-nitrophenylhydrazone-2-phenylhydrazone.*—This was prepared by heating benzilmono-p-nitrophenylhydrazone with an equivalent amount of phenylhydrazine or by heating benzilmonophenylhydrazone with p-nitrophenylhydrazine. It crystallised from hot acetic acid, m.p.  $255^{\circ}$ . (Found: N, 16.0.  $C_{26}H_{21}O_2N_5$  requires N, 16.09 per cent).

*Condensation of hydroxymethylenephénylethylketone and diazo-benzene chloride: Formation of a monophenylhydrazone of acetylbenzoyl.*—The condensation product was separated in the usual way. It crystallised from dilute alcohol as pale yellow needles, m.p.  $146-47^{\circ}$ . It is soluble in alcohol and acetic acid. (Found: N, 12.06.  $C_{15}H_4ON_2$  requires N, 11.76 per cent).

*1-p-Nitrophenylhydrazone-2-phenylhydrazone of acetylbenzoyl* was prepared by heating the monophenylhydrazone of acetylbenzoyl with an equivalent quantity of nitrophenylhydrazine in glacial acetic acid solution on the water-bath for  $\frac{1}{2}$  hour and crystallised from hot acetic acid as deep red needles, m.p.  $230^{\circ}$ . (Found: N, 18.5.  $C_{21}H_{19}O_2N_3$  requires N, 18.97 per cent).

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## Hydrolysis of Chloro-, Ethoxy- and Methoxy-2-cyano-4-nitrobenzenes.

BY BIMAN BIHARI DEY AND YETCHAN GUNJA DORAISWAMI.

The methods commonly employed for the hydrolysis of substituted aromatic nitriles may be classified as follows:—

(a) Hydrolysis by boiling with dilute sulphuric acid; Claus and Kurz (*J. pr. Chem.*, 1888, ii, 37, 196) have by this method hydrolysed *p*-chloro-*m*-nitro-, *p*-chloro-*o*-nitro- and *m*-chloro-*o*-nitro-benzonitriles into the corresponding acids. In many cases, however, action proceeds no farther than the formation of the acid amide (*vide* Küster and Stallberg, *Annalen* 1894, 278, 207, regarding hydrolysis of nitro- $\beta$ -isoduronitrile)

(b) Hydrolysis by heating with concentrated hydrochloric acid under pressure; Küster and Stallberg (*loc. cit.*) have thus hydrolysed nitro- and dinitro- $\beta$ -isoduronitrile by heating with concentrated hydrochloric acid in sealed tubes at about 200°

(c) Digestion of the nitrile with 85 or 90% sulphuric acid at 100° (*cf.* Bouveault, *Bull. Soc. chim.*, 1892, iii, 9, 368). when the amide is formed, the conversion into acid being effected by dissolving the amide in cold strong sulphuric acid and adding the requisite amount of cold concentrated sodium nitrite at 30°, finally warming for a few moments to 40-50°. Sudborough's method (*J. Chem. Soc.*, 1895, 67, 601) is a modification of Bouveault and consists in heating the nitrile with a large excess of 90% sulphuric acid for 1 hour at 120-3°, adding to the well cooled solution the theoretical amount of sodium nitrate and warming on the water-bath until effervescence ceases

(d) The method of Berger and Olivier (*Rec. trav. Chim.*, 1927, 46, 600) who find that 2:6-dimethylbenzonitrile, which is not hydrolysed by 90% sulphuric acid or even by methyl or amyl alcoholic potash, is hydrolysed by concentrated sulphuric acid merely to 2:6-dimethylbenzamide, this amide being hydrolysed into the acid only by 100% phosphoric acid at 145-50°.

The method found most convenient by the authors for the hydrolysis of 1-chloro-, 1-ethoxy- and 1-methoxy-2-cyano-4-nitrobenzenes is described in the experimental section.

1-Chloro-2-cyano-4-nitrobenzene is hydrolysed by sulphuric acid first into 2-chloro-5-nitrobenzamide and the latter, on boiling with hydrochloric acid, yields 2-chloro-5-nitrobenzoic acid. The nitrile, the amide and the acid, on boiling with aqueous or alcoholic potash, yield 5-nitrosalicylic acid, a conversion which has also been noticed in the case of the acid by Purgotti and Contardi (*Gazzetta*, 1902, i 32, 526).

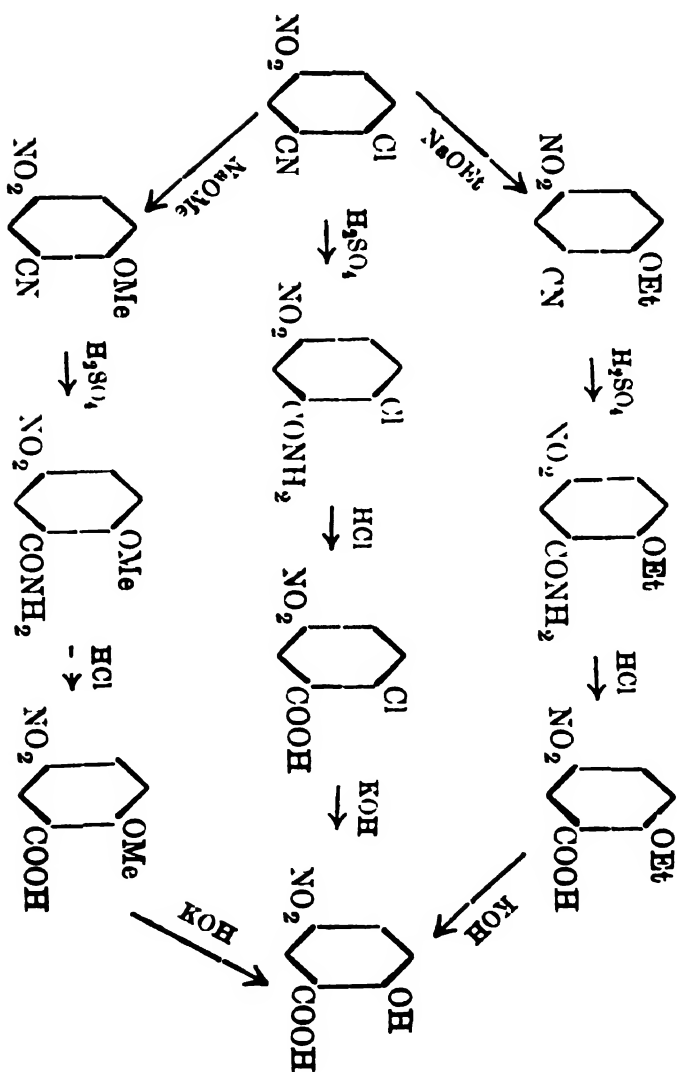
Ethoxy- and methoxy-2-cyano-4-nitrobenzenes are similarly hydrolysed by sulphuric acid into 2-ethoxy-5-nitrobenzamide and 2-methoxy-5-nitrobenzamide respectively. They are hydrolysed by hydrochloric acid respectively into 2-ethoxy-5-nitrobenzoic acid previously made by Perkin (*Annalen*, 1868, 145, 312) by nitration of *o*-ethoxybenzaldehyde, and by Kraut (*Annalen*, 1869, 180, 4) by nitration of *o*-ethoxybenzoic acid and 2-methoxy-5-nitrobenzoic acid previously made by Kraut (*loc. cit.*) and Salkowski (*Annalen*, 1874, 173, 41) by nitration of *o*-methoxybenzoic acid, and by Hale and Robertson (*Amer. Chem. J.* 1908, 39, 688) by permanganate oxidation of 2-acetyl-4-nitrophenol-methylether. The ethoxy- and methoxynitrobenzonitriles, the amides and the acids are all converted by caustic potash into 5-nitrosalicylic acid.

The series of observations mentioned above may be conveniently represented by the scheme shown in the next page

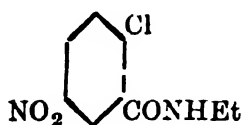
It would not be out of place to mention here that whereas 1-chloro-2-cyano-4-nitrobenzene is hydrolysed by strong sulphuric acid or hydrochloric acid or caustic potash, none of these agents is able to hydrolyse 1-chloro-2-cyano-4-aminobenzene obtained by the reduction of 1-chloro-2-cyano-4-nitrobenzene. This interesting observation seems to show how the substitution of the nitro group in chloro-2-cyano-4-nitrobenzene by an amino group renders the hydrolysis of the CN group extremely difficult. The Cl atom, moreover, cannot be knocked off from the nucleus by means of caustic potash.

Several interesting derivatives of 2-chloro-5-nitrobenzoic acid have been prepared, incidentally, during the study of the reactivity of the chlorine atom in this compound. These derivatives have been made through the acid chloride, the latter being most conveniently obtained by the action of thionyl chloride on the acid: this method

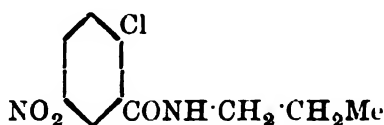




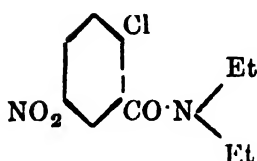
gives a far better yield than that of Montagne (*Rec. trav. Chim.*, 1900, 19, 57). The several amides were made by shaking an aqueous suspension of the acid chloride with various amines, *e.g.*, ethyl amine (III), propylamine (IV), diethylamine (V), ethylenediamine (VI), etc., while the ureide (VII) was obtained by fusing the chloride with urea.



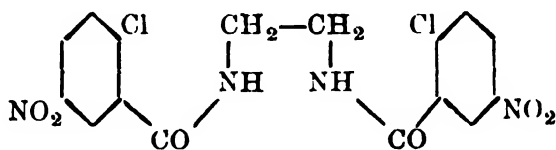
(III)



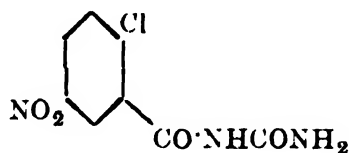
(IV)



(V)

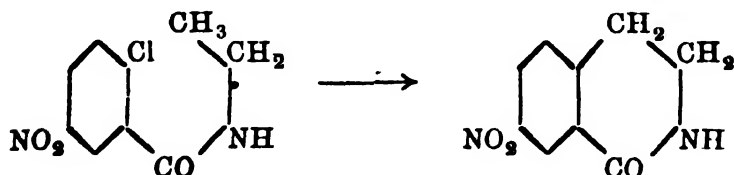


(VI)



(VII)

These amides were prepared in the hope that the reactive chlorine atom might be made to interact with a hydrogen atom of the alkyl group, leading to the closure of an *isoquinoline* ring thus:



Repeated attempts made in this direction, however, using such agents as copper dust,  $\text{AlCl}_3$ ,  $\text{PbO}$ ,  $\text{POCl}_3$ , etc., failed to give the desired result. The amides were found to be extremely stable, the ethylamide, for example, being recovered unchanged even after vigorous boiling with  $\text{PCl}_5$  and  $\text{POCl}_3$  for several hours.

## EXPERIMENTAL.

*Hydrolysis of the Chloro-, Ethoxy- and Methoxynitrobenzonitriles.*

A. 1-Chloro-2-cyano-4-nitrobenzene. *Hydrolysis with  $H_2SO_4$ : 2-Chloro-5-nitrobenzamide.*—Chlorocyanonitrobenzene (2 g.), moistened with 10-12 drops of water, was slowly treated with conc. sulphuric acid (10 c.c.). The slightly coloured, clear warm liquid was heated over a free flame to simmer for about 10 minutes until it just began to fume, and poured after half an hour into cold water (50 c.c.). The precipitate crystallised from boiling water (with the addition of a few c.c. alcohol) in shining white needles, m.p.  $178^\circ$ , yield about 2 g. This product had been obtained by Montagne (*loc. cit.*) by the action of aqueous ammonia on 2-chloro-5-nitrobenzoyl chloride.

On boiling with 10% caustic potash, the amide went into a clear yellow solution, with the evolution of ammonia and the formation of 5-nitrosalicylic acid (m.p.  $228^\circ$ ).

*Hydrolysis of the amide with HCl: 2-Chloro-5-nitrobenzoic acid.*—Chloronitrobenzamide (2 g.) was boiled with conc. HCl (10-12 c.c.) on a wire gauze for an hour. On cooling, the product separated from the clear liquid and was purified by recrystallisation from boiling water, (m.p.  $164^\circ$ ). On boiling this acid with 10% potash 5-nitrosalicylic acid was obtained.

## B. 1-Ethoxy-2-cyano-4-nitrobenzene.

*Hydrolysis with  $H_2SO_4$ : 2-Ethoxy-5-nitrobenzamide.*—1-Ethoxy-2-cyano-4-nitrobenzene was hydrolysed with  $H_2SO_4$  just as in the previous case. The product crystallised from dilute alcohol in small white needles, m.p.  $176^\circ$ . (Found: N, 13.51.  $C_9H_{10}O_4N_2$  requires N, 18.84 per cent).

2-Ethoxy-5-nitrobenzoic acid was prepared by boiling 2-ethoxy-5-nitrobenzamide with concentrated HCl for 1 hour as in the previous case and crystallised from dilute alcohol in almost white needles, m.p.  $162^\circ$ . (Found: N, 6.71. Calc.: N, 6.63 per cent).

Boiling with potash converted both the amide and the acid into 5-nitrosalicylic acid (m.p.  $228^\circ$ ).

## C. 1-Methoxy-2-cyano-4-nitrobenzene.

*Hydrolysis with  $H_2SO_4$* : 2-Methoxy-5-nitrobenzamide (II), obtained just as in the case of the ethoxy analogue by sulphuric acid hydrolysis of the corresponding nitrile, melted at  $212^\circ$ . (Found: N, 14.13.  $C_8H_8O_4N$  requires N, 14.33 per cent).

2-Methoxy-5-nitrobenzoic acid was similarly obtained by boiling 2-methoxy-5-nitrobenzamide with concentrated HCl for 1 hour, m. p.  $151^\circ$ . (Found: N, 7.28. Calc.: N, 7.11 per cent).

Boiling with caustic potash converted both the amide and the acid into 5-nitrosalicylic acid (m. p.  $228^\circ$ ).

*Derivatives of 2-Chloro-5-nitrobenzoic Acid.*

2-Chloro-5-nitrobenzoyl chloride.—Chloronitrobenzoic acid (30 g.), mixed with excess of thionyl chloride (40 g.), was heated on a water-bath in the usual way until no more HCl fumes were given off. The clear liquid was now distilled from the water-bath under reduced pressure, when it solidified to a crystalline mass. The last traces of thionyl chloride were removed by washing with ice-water and the product dried on a plate in a vacuum desiccator. Colourless cube-shaped crystals, m.p.  $59^\circ$ , yield 28 g. This substance had been obtained in a much poorer yield by Montagne (*loc. cit.*) by the action of  $PCl_5$  on chloronitrobenzoic acid.

2-Chloro-5-nitrobenzamide (*cf.* Montagne, *loc. cit.*).—On shaking a suspension of the chloride in water with aqueous ammonia, the amide was formed crystallising from water in white needles, m.p.  $176^\circ$ , identical with the product obtained by the hydrolysis of chloro-2-cyano-4-nitrobenzene with  $H_2SO_4$ .

The *methylamide* (*cf.* Montagne, *loc. cit.*) was obtained by similarly shaking a suspension of the chloride in water with methylamine (33% aqueous or alcoholic solution), m.p.  $171^\circ$ .

The *ethylamide*.—The chloride (2 g.), finely suspended in water (10 c.c.), was slowly treated in the cold with ethylamine (33%, 5 c.c.), the mixture shaken for 1 hour and the cream-coloured precipitate crystallised from boiling water with the addition of a little alcohol as glistening white flakes, m.p.  $148^\circ$ , yield 1.7 g. (Found: N, 12.35.  $C_9H_9O_3N_2Cl$  requires N, 12.25 per cent).

The *propylamide*, prepared from the chloride and propylamine, crystallised from boiling water in shining flakes, m.p.  $142^\circ$ . (Found: N, 11.78.  $C_{10}H_{11}O_3N_2Cl$  requires N, 11.55 per cent).

The *2-diethylamide*, prepared by the action of diethylamine on the chloride, crystallised from alcohol in pale yellow needles, m.p. 72°. (Found: N, 11.19.  $C_{11}H_{13}O_2N_2Cl$  requires N, 10.29 per cent).

The *ethylenediamide* was obtained as a white amorphous powder from the chloride and ethylenediamine. It could not be crystallised from any suitable solvent and was purified by washing with hot acetic acid, m.p. 310°. (Found: N, 13.29.  $C_{16}H_{12}O_6N_4Cl_2$  requires N 13.11 per cent).

The *ureide*.—The chloride (2 g.) and urea (1.5 g.) were warmed together on the free flame when the mixture melted and reacted vigorously with the evolution of  $NH_4Cl$  fumes. Carbon tetrachloride (10 c.c.) was added and the paste thoroughly mixed and heated again (5-10 minutes). The product was filtered, washed with methanol and crystallised from acetic acid as clusters of hard, perfectly white needles, m.p. 216°. (Found: N, 17.53.  $C_8H_6O_4N_3Cl$  requires N, 17.25 per cent).

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## Vitamin A in Fish Liver Oils.

By P. N. CHAKRAVORTY, H. C. MOOKERJEE AND B. C. GUHA.

A systematic investigation of the vitamin A-potency of Indian fish liver oils does not appear to have been undertaken. Recent observations in other countries on various fish-liver oils including halibut, mackerel and sturgeon liver oils, which have been found to be much more potent in vitamin A than cod liver oil, indicate the possibility of there being large vitamin A reserves in the liver oils of certain Indian fishes also. It is with this possibility in mind that the present investigation was undertaken. We have commenced this work with the liver oils of fishes commonly consumed in Bengal and we expect to send further communications on the subject.

### *The Assay of Vitamin A in Liver Oils.*

The Carr-Price colorimetric method (*Biochem. J.*, 1926, 20, 497) was adopted for the estimation of vitamin A in the liver oils. Results of the biological tests, which are being carried out, will be reported later.

Within the last few years, however, doubt has been cast on the reliability of the colorimetric method for the assay of vitamin A. Schmidt-Nielsen (*Kon. Norsk. Videnskab. I.*, No. 15, 29, 63) has reported that 'the tintometric and biological tests do not give concordant values for the body and liver oils of certain marine fishes. Ahmad and Drummond (*Biochem. J.*, 1930, 24, 27), on the other hand, have concluded from a reinvestigation of the subject that for fish oils the tintometric method gives reliable values. Ender (*Biochem. J.*, 1932, 26, 1118) and Norris (*Bull. Basic. Sci. Res.*, 1931, 3, 89, 249) have recently given some noteworthy evidence to show that the chromogen concerned is not necessarily identical with vitamin A. Our own results indicate that in the fish liver oils under our investigation, there is probably more than one chromogen present (*cf.* Gillam and Morton, *Biochem. J.*, 1931, 25, 1346), so that the blue values, we report, should be accepted with reserve as a measure of vitamin A values.

*Preparation of the materials.*—The finely minced liver was ground up with excess of anhydrous sodium sulphate and extracted repeatedly with ether in the cold. The ethereal extract was evaporated by means of an electric fan and the oil obtained. Generally the oils were coloured, varying from deep yellow to yellow-brown. The oils were fairly mobile, getting more and more viscous on standing. They had their peculiar odours, the smell of *Mrigal* liver oil being strongly suggestive of cod liver oil.

*Technique of the colorimetric experiments.*—As described by Carr and Price (*loc. cit.*) the liver oil (about 2 g.) was dissolved in chloroform (10 c.c.) dried over anhydrous potassium carbonate. 0.4 C.c. of the solution and 4 c.c. of a saturated solution of  $\text{SbCl}_3$  in anhydrous chloroform were used for each observation made with a Lovibond tintometer of the B.D.H. pattern. The maximum development of the colour usually took place in about 30 seconds. Matching was always carried out with a standard artificial light.

As intensely deep colours could not be accurately matched, it was found necessary to use very dilute solutions in some cases for tintometric examinations. The relation between the dilution and intensity of colour produced is approximately linear only within a small range. The Carr-Price blue values obtained in this investigation have, however, been computed on the assumption of such a linear relation. The actual deviation from this relation will be observed from the following experiment carried out with *Mrigal* liver oil.

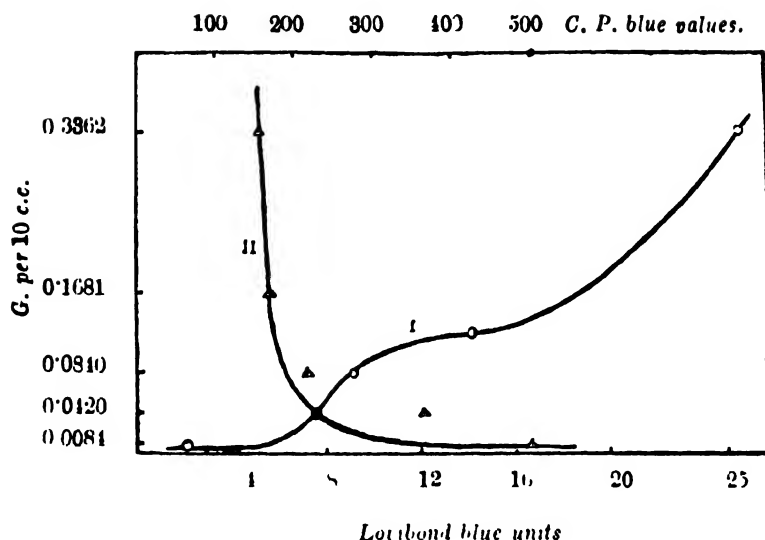
*Relation between the dilution of Mrigal liver oil and the intensity of the colour produced.*—In Fig. 1, curve (I) shows the relation between the observed colour intensity and the concentration of the liver oil. Curve (II) has been obtained by plotting the Carr-Price values calculated from the respective blue value readings against the concentration of the oil.

It will be seen from curve (I) that the relation between the concentration and the intensity of the colour is linear within a short range and that, where the concentration is relatively higher. At a lower concentration the divergence is very great.

At higher concentrations the C.P. value-concentration curve (Curve II) is parallel to the ordinate which shows that the relation between the concentration and intensity is linear within this range. At lower concentrations the Carr-Price value goes up as high as 500, while the Carr-Price value of the same oil, calculated from readings



FIG. I.



at a higher concentration, is only 216. Thus Carr-Price values obtained from readings at low concentrations are apt to be very misleading.

From these considerations it would seem desirable to observe the blue values of oils at higher concentrations. But the values obtained at these concentrations are generally much above 15 Lovibond units and hence the matching becomes inaccurate. Thus the apparent advantage gained by choosing a concentrated solution for testing is somewhat negated by inaccurate matching.

We have, therefore, accepted a *via media*. The concentration chosen falls roughly within the range where the intensity-concentration relation may be taken to be linear. Within this range the values observed are not too high for accurate matching.

#### *The Blue Values of the Fish Liver Oils.*

1. *Halibut liver oil*.—0.6180 G of the oil dissolved in  $\text{CHCl}_3$  gave a very intense coloration with the  $\text{SbCl}_3$  reagent, 0.5 c.c. of the chloroform solution was then diluted with chloroform to 10 c.c. so that the final solution contained 0.0309 g. of the oil in 10 c. c.

Obs.	Blue units.	Yellow units.	Neutral tints.
1	9.5	3.4	2
2	9.5	3.5	2
3	9.5	3.5	2
4	9.6	3.5	2
Mean 9.5			

Carr-Price blue value— 614.8.

2. *Rohit (Labeo rohita) liver oil*.—130 G. of fresh *Rohit* liver gave 3.108 g. of a yellowish brown oil. The sample of liver was collected in the earlier part of March. 1.1430 G. of the oil in 10 c.c. chloroform gave a rather intense coloration and 1 c.c. of the above solution was diluted with chloroform so that the solution contained 0.1143 g. of oil in 10 c.c.

Obs.	B	Y	N
1	12.9	4.5	0.4
2	12.9	4.5	0.4
3	12.9	4.5	0.4
Mean 12.9			

Carr-Price blue value— 226.6.

Another sample of liver collected in early May gave 5.822 g. of oil from 235 g. of liver. 0.17 G. in 10 c.c. chloroform gave the following values.

Obs.	B	Y	N
1	13.7	2.4	0.2
2	13.7	2.4	0.3
3	13.8	2.4	0.3
Mean 13.7			

Carr-Price blue value—161.1.

3. *Mrigal (Cirrhina mrigala) liver oil*.—265 G. of *Mrigal* liver, collected in early May, gave 15.714 g. of a dark brown mobile oil.

0.1663 G. of the oil dissolved in 10 c. c. of chloroform was used for tintometric tests.

Obs.	B	Y	N
1	14.1	2.9	0.1
2	14.1	2.9	0.4
3	14.6	2.9	0.6
4	14.6	3.0	0.6
5	14.7	3.1	0.6

Mean 14.5

Carr-Price blue value—171.4.

4. *Katla (catla catla) liver oil*.—115 G. of *Katla* liver, collected in early May, gave 7.876 g of a mobile golden yellow oil 0.2 G. of oil dissolved in 10 c.c. of chloroform was used for tintometric observations

Obs	B	Y	N
1	10.2	2.8	0.2
2	11.2	2.9	0.2
3	11.4	2.9	0.3

Mean 10.9

Carr-Price value—109.

5 *Hilsha (Clupea Ilisha) liver oil*—137 G. of *Hilsha* liver gave 4.213 g. of a golden yellow oil, containing some waxy substance. 0.3 G. of the oil in 10 c.c. of chloroform was used.

Obs.	B	Y	N
1	8.9	2.9	0.7
2	8.8	3.0	0.7
3	9.0	3.0	0.7
4	9.0	3.3	0.7

Mean 8.8

Carr-Price blue value—59.

6. *Vetki (Lates calcarifer) liver oil*.—55 G. of *Vetki* liver gave 1.278 g. of a viscid yellow oil. The sample was collected in late May.

0.05 G. of oil dissolved in 10 c.c. of chloroform gave the following values.

Obs	B	Y	N
1	7.0	2.8	...
2	7.1	2.7	0.1
3	7.1	2.8	0.1
4	7.1	2.9	0.1

Mean 7.1.

Carr-Price blue value—284.

7. *Cod liver oil*.—1.8 G. of cod liver oil (B.C.P.W.) dissolved in 10 c.c. of chloroform were used. A sample of cod liver oil of Norwegian origin was also tested for vitamin A-potency, 1.9 g. of the oil dissolved in 10 c.c. chloroform being used.

B. C. P. W.			Norwegian.		
Obs.	B	Y	Obs.	B	Y
1	4.0	0.4	1	5	0.7
2	3.9	0.4	2	5	0.8
3	3.9	0.4	3	5	0.8
Mean	3.9			Mean 5.0	

Carr-Price blue value—4.3.

Carr-Price blue value—5.2

The copious mesenteric fat of *Rohit* was found to be devoid of vitamin A both by tintometric and biological tests.

#### SUMMARY.

Liver oils of *Rohit*, *Mrigal*, *Katla*, *Vetki* and *Hilsha* fishes have been tested for vitamin A-potency by the tintometric method. Their blue values are of the order of 227, 174, 109, 284 and 59 respectively. Another sample of *Rohit* liver oil, obtained from the liver collected at a different time, gave a blue value of 161, indicating that seasonal variations in vitamin A-content may be considerable. Comparison with two samples of commercial cod liver oil of average activity having blue values of 4.3 and 5.1 indicates the relative richness of the above Indian fish liver oils in vitamin A. The tintometric examination of a sample of halibut liver oil gave a blue value of 614.

# **Studies in the Protective Action of Colloids. Part III. Influence of Sucrose and Sodium Oleate on the Stability of Colloid Manganese Dioxide.**

BY SHRIDHAR SARVOTIAM JOSHI AND AVADH NARAYAN LAL.

It was observed previously (Joshi and Lal, *J. Indian Chem. Soc.*, 1933, 10, 63) that presence of sucrose did not affect sensibly the kinetics of coagulation of the above sol by potassium and barium chloride. Further work showed that this sol was coagulated under certain conditions, by the addition of sucrose, which is interesting. While a number of electrolytes are known to sensitise, that is, to increase the coagulative power of the electrolyte added, coagulation and the concomitant change of properties initiated by substances like sugar alone appear to have been hitherto examined not in detail. The present paper records work carried out with sucrose and sodium oleate from the view point just mentioned.

## **EXPERIMENTAL.**

The sol was prepared, and its colloid content estimated as described in the previous paper (*loc. cit.*). The last quantity before mixing with the solutions of the protector was 0.75 g. of  $\text{MnO}_2$  per litre in all the experiments. The sol having been prepared by Cuy's method (*J. Phys. Chem.*, 1921, 25, 415) contained traces of KOH. In view of the fact that viscosity reveals perhaps to the greatest extent but small changes produced in colloid, the above action of the protector added in different proportions was studied by measuring variations in this property. The experimental arrangement of measuring viscosity was that due to Scarpa (*Gazzetta*, 1910, 40, 271; cf. also Farrow, *J. Chem. Soc.*, 1912, 101, 347) with modifications described in a previous paper (this number, Joshi and Viswanath, p. 329). The temperature of the thermostat in all the experiments was 35°. The solutions of sucrose and sodium oleate used were made from Merck's guaranteed pure materials. Viscosity was measured 15 minutes after mixing the colloid with any of the protecting solutions. Measurement of viscosity was repeated at least twice and the results

agreed within 0.1% in each case. This observation was taken soon after mixing, since after long periods of time, conglutination occurred in some of the solutions and then the corresponding value of viscosity was less reproducible than above. The viscometer used in experiments with sodium oleate (Tables III, IV) was different from that used with sucrose solutions (Tables I, II).

TABLE I.

Protector used = 50% sucrose.

No.	Composition of the mixture			$t_1$ .	$t_2$ .	Visco- sity.	Remarks.
	Sol.	Sugar.	Water.				
1	16 c. c.	4 c. c.	...	7' 35"	5' 20"	1.181	The sol. coagulated appreciably after 24 hrs. The corresponding value was 1.21
2	„	3	1 c. c.	6' 47"	5' 3"	1.123	
3	„	2	2	6' 34"	4' 51"	1.082	
4	„	1	3	7' 26"	4' 59"	1.178	

TABLE II.

Protector used = 25% sucrose.

1	„	4	...	7' 15"	5' 2"	1.18	Slight coagulation observed after 24 hrs.
2	„	3	1	5' 50"	4' 47"	1.018	
3	„	2	2	5' 25"	4' 10"	0.915	
4	„	1	3	6' 20"	4' 52"	1.07	

TABLE III.

Protector used = 0.334%, sodium oleate.

	Sol.	Sodium oleate.	Water.	$t_1$ .	$t_2$ .	Visco- sity.	
1	10 c. c.	10 c. c.	...	1' 35"	2' 21.4"	0.757	Coagulates after about $\frac{1}{2}$ hr.
2	„	8	2	1' 33"	2' 20"	0.711	Coagulates after about 1 hr.
3	„	6	4	1' 32.4"	2' 19"	0.741	Coagulation observed to be appreciable after only 24 hrs.
4	„	5	5	1' 32.2"	2' 20"	0.742	
5	„	4	6	1' 34"	2' 18"	0.745	
	„	3	7	1' 34.6"	2' 18.5"	0.749	
7	„	2	8	1' 35"	2' 19"	0.752	

TABLE IV.

Protector used = 0.167% sodium oleate.

No.	Sol.	Sodium oleate. 10 c. c.	Water. ...	$t_1$ .	$t_2$ .	Vis- cosity. 0.599	Remarks.
1	10 c. c.	10 c. c.	...	1' 10"	2' 5 9"	0.599	Coagulates in about 2 hrs.
2	..	8	2 c. c.	1' 8"	2' 4"	0.565	Coagulates after about 24 hrs
3	..	6	4	1' 7"	2' 3 1"	0.578	
4	..	5	5	1' 6.8"	2' 4.4"	0.58	
5	..	4	6	1' 7.5"	2' 4.8"	0.58	
6	..	3	7	1' 7.7"	2' 5'	0.585	
7	..	2	8	1' 8.1"	2' 5.1"	0.587	

## DISCUSSION.

For its well known capillary activity, its high 'gold number', and such allied properties as its detergent and peptising action, sodium oleate is regarded, in general, as a typical protecting agent. The coagulation of the sol on its admixture is, therefore, interesting, and particularly the fact that this effect is greater at larger proportions of sodium oleate. With lower amounts of the latter, the sol remained unchanged for at least 48 hours. These results suggest an interrelation, perhaps a possible merging of a protector with a coagulator under change of conditions, here simply by increasing the concentration of the oleate added. In this connection it is interesting to point out that faintly acid Donau gold sol, or a Carey Lea silver sol is coagulated upon the addition of but small amounts of gelatine, the last being freed of electrolytes as much as possible (Freundlich, "Colloid and Capillary Chemistry," Eng. Trans., 1926, pp. 582-583). This has been ascribed by Freundlich and Löning (*loc. cit.*, p. 585) to the presence of oppositely charged colloid ions present in such hydrophiles. With the exception of our observation that the coagulating effect diminishes by reducing the concentration of sodium oleate added, the above explanation would appear in the main to be applicable to our results, since the existence of colloid ions in soap solutions is now well recognised.

The last factor is absent in sucrose solutions, and coagulations due to them (Tables I, II) cannot, therefore, be explained on the above

view. This type of change would appear to be classifiable with the so-called sensitisation, produced in general by soluble non-electrolytes. The pioneer work in this field is by Kruyt and van Duin (*Koll. Chem. Beih.*, 1914, 5, 269), Wo. Ostwald, who was the first to emphasise the variability of the dielectric constant in such cases (*cf.* Freundlich and Rona, *Biochem. Z.*, 1917, 81, 87), Cussuto (*cf.* Weiser, *J. Phys. Chem.*, 1924, 28, 1253) and especially Freundlich ("Colloid and Capillary Chemistry," p. 463). Freundlich proceeds on the simple assumption of an analogy of a colloid particle enclosed in the 'Helmholtz double layer', with a charged condenser. Since non-electrolytes usually possess comparatively low dielectric constants, their adsorption would lead to a diminution of the last quantity. A reduction in the charge, the stability of the colloid particle and therefore, in the adsorption of the opposite ions required for coagulation, is to be anticipated as a necessary consequence. The insufficiency of this view is shown by the work of Rona and György (*Biochem. Z.*, 1920, 105, 133), Weiser (*loc. cit.*), Sen (*Kolloid Z.*, 1926, 38, 310) and Mukherjee, Chaudhury and Roy Choudhury (*J. Indian Chem. Soc.*, 1927, 4, 493, *et seq.*). It is seen that changes in dielectric constant alone can not be considered as the sole determinant of sensitisation. Furthermore, it is tacitly assumed in Freundlich's theory that sensitisation is necessarily preceded by the adsorption of the non-electrolyte on the colloid by virtue of its capillary activity.

The difficulty of applying the last postulate to our results with sugar is evident from the observation of Bhatnagar, Srivastav and Gupta (*Kolloid Z.*, 1925, 37, 101) that the adsorption of sugar on  $\text{MnO}_2$  is but insensible. It would also appear from a survey of the literature that a marked capillary activity is not necessarily the characteristic of a sensitizer. Moreover, this action is a specific one both as to the nature of the non-electrolyte and the coagulator. Thus for example, Sen (*loc. cit.*) has observed, in the coagulation of the  $\text{MnO}_2$  sol by copper sulphate and silver nitrate in the presence of ethyl alcohol and sucrose, that the former stabilises the sol against copper sulphate more than silver nitrate. Also, using the last electrolyte, sucrose did not exert any appreciable effect, as we found previously in coagulations by potassium and barium chloride (Joshi and Lal, *loc. cit.*). A further important element in Freundlich's theory is that sensitizers do not initiate coagulation but merely augment it due to added electrolytes (Freundlich and Rona, *loc. cit.*; Rona and György, *loc. cit.*).



The observation of Freundlich that no alteration is produced even after long time when the arsenious sulphide sol is mixed with a number of non-electrolytes added in large concentrations (*Z. physikal. Chem.*, 1903, **44**, 136) is at variance with that of Klein (*Kolloid Z.*, 1921, **29**, 247) who observed coagulation in the above and other colloids by the addition of non-electrolytes, in the absence of any added electrolytes. Similarly Billitzer (*Z. physikal. Chem.*, 1903, **45**, 812) using a platinum sol and Wo. Ostwald (*cf.* Weiser, *loc. cit.*) using a silver sol observed that they can be coagulated by adding suitable amounts of alcohols. Recently Patel and Desai (*Kolloid Z.*, 1930, **51**, 318) observed that a long dialysed thorium hydroxide sol can also be coagulated by non-electrolytes alone. In the main, these results would appear to be in line with ours (Tables I, II), and are to be ascribed to the appreciable alteration of the nature of the dispersion medium.

It is very interesting to note the initial fall of viscosity at low proportions of the sodium oleate and sugar added. A strikingly similar diminution of viscosity has been noted by a number of workers when a given volume of colloid is treated with successively small increments of electrolytes (Gokun, *Z. Chem. Ind. Kolloid*, 1908, **3**, 84; Woudstra, *ibid*, 1911, **8**, 73; Farrow, *loc. cit.*; Dhar and Chakravarti, *J. Phys. Chem.*, 1926, **30**, 1646). In view of the lack of a definite knowledge of the factors which determine completely the viscosity of a colloid, it is not surprising to note the diverse, and at places conflicting explanations of the above phenomenon by different workers; more experimental work is needed to elucidate it. Meanwhile it is interesting to note the occurrence of the same effect in the presence of a non-electrolyte and a typical protecting agent like sodium oleate.

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## Optical Activity of Alkaloid Salts of Geometrically Isomeric Unsaturated Acids.

BY PANCHANAN NEOGI AND ANIL BEUSAN SEN-GUPTA.

The relation between geometrical isomerism and optical activity was first studied by Walden (*Z. physikal. Chem.*, 1896, **20**, 377) who observed that in the case of diamyl esters of maleic and fumaric acids, chloro- and bromomaleic and chloro- and bromofumaric acids the fumaroid possessed the greater rotatory power, but Hartwall (Dissertation, Helsingfors, 1904) found the reverse rule to hold for the acid and neutral bornyl esters of maleic and fumaric acids, although with both menthyl and bornyl acid citraconates and mesaconates the fumaroid possessed greater rotatory effect.

Hilditch (*J. Chem. Soc.*, 1908, **61**, 704) from a study of several alkaloid salts (conine, codine, brucine and cinchonine) of maleic and fumaric acids obtained results in chloroform solutions which with some few exceptions showed that the malenoid forms had greater specific rotations than the fumaroid.

It appeared to us that a larger amount of experimental work should be forthcoming to establish, if possible, a general rule regarding the relative optical activity of active geometrical isomers and therefore we undertook a systematic study of the rotations of a large number of alkaloid salts of ethylinic dicarboxylic acids.

The alkaloids used in the work described were quinine, brucine, quinidine, strychnine and cinchonidine, and the rotatory power of the salts of these with maleic and fumaric acids, citraconic and mesaconic as well as crotonic and isocrotonic acids has been measured. The solvent generally employed was dry alcohol, in a few cases it was necessary to have recourse to chloroform. Owing to the great ionising influence of water, aqueous solutions were not employed.

It appears from the present investigation that in the case of alkaloid salts of unsaturated isomeric ethylinic acids it can be formulated as a general rule that the specific rotations of the malenoid type is almost always greater, bearing some exceptions observed by

Hilditch (*loc. cit.*), than that of the fumaroid form and that the specific rotations of the alkaloid salts and amyl esters of the ethylinic dicarboxylic acids are relatively reverse of each other. So far as the effect of dilution is concerned it is of interest to note that with increase in dilution the specific rotation decreases. The rotations were obtained in non-ionising media, *vis.*, alcoholic and chloroformic solution and hence it is not strange if reverse results are obtained to those of Oudemans and Landolt (*Annalen*, 1876, 182, 33, 58; *Ber.*, 1873, 6, 1077) who showed that in ionising media such as in aqueous solutions the rotations increased and were approximating those of the active ions on continuous dilution owing to ionisation.

The influence of solvents on optical activity has been studied by many investigators and various theories have been put forward to explain the anomalous behaviour of rotations in different solvents. But so far as the effect of concentration on rotation is concerned no satisfactory explanation is found in literature. Graham (*J. Chem. Soc.*, 1912, 101, 746), who has shown that Oudemans-Landolt law is not universally applicable, suggested that the change observed was not dependent on the electrolytic dissociation alone but depended principally on the character of the metallic atom or electropositive grouping, since similar effects were produced by members of the same group in the periodic table. Armstrong and Walker (*Proc. Roy. Soc.*, 1913 88A, 388) are of opinion that the cause of the variation in the optical rotatory power of organic compounds and anomalous rotatory dispersion may be ascribed to (a) alteration in the molecular size and to the formation of compounds between solvents and the solute, (b) to the occurrence of change giving rise to the presence of reversibly related isodynamic forms.

The decrease of the specific rotations of the salts with increase in dilution in non-ionising media might be supposed to be due to the formation of some compounds of the solute with the solvent employed, and that with increase in dilution the proportion of the molecules existing in the combining state increases thus causing a diminution in the proportions of active molecules. It was not possible to have direct evidence in support of this view by determining the molecular weight of the salt at different concentrations in alcoholic or chloroformic solution by the freezing point method owing to very low freezing point of alcohol or chloroform. The boiling point method is obviously inapplicable owing to possibility of decomposition. The substances are insoluble in benzene. The

suggestion, therefore, remains a tentative one so long as direct evidence is not forthcoming.

No generalisation as regards the magnitude of the increase of the specific rotations of the malenoid type over the fumaroid form is possible. In most cases, however, using maleic and fumaric acids the increase is between five to ten degrees, in the case of citraconates and mesaconates the increase is between three to twelve degrees, and finally in the case of crotonates and isocrotonates it is between four to seven degrees. This is only a rough approximation as individual variations in equal dilutions are sometimes besides the limit mentioned above.

#### EXPERIMENTAL.

*General method of the preparation of the salts.*—Alcoholic solutions of the base (2 mol.) and the acid (1 mol.) were mixed together and allowed to evaporate slowly, when solid crystals separated. The crystals were filtered and purified by washing with hot acetone in which the alkaloids and the acids were soluble but the salts insoluble. The salts were finally recrystallised from hot alcohol or water as colourless needles.

The isomeric salts differ from each other in melting points, solubility and sometimes in the shape of crystals.

The salts decolourise rapidly dilute permanganate solution and bromine water, thus showing the presence of unsaturation. They are insoluble in sodium bicarbonate solution (hot or cold) proving the absence of free carboxyl group and all of them are neutral to litmus paper showing the formation of dialkaloidal salts. The alkaloidal salts are described in Table I.

Alcoholic solutions of the same concentration of the isomeric salts were prepared and the rotations were measured in a 2 dm. tube keeping the temperature constant by circulating water at constant temperature through the tube. From the rotations thus observed the specific rotations were calculated. The rotations at different dilution are given in Table II.

TABLE I.

Name.	Formula	M. p.	Found	Analysis.	Calc.
Diquinine maleate	$(C_{20}H_{24}N_2O_2)_2C_4H_4O_4$	182-83°	C, 68.79; H, 7.11; N, 7.59		C, 69.1; H, 6.8; N, 7.32
Diquinine fumarate	"	187-88°	C, 68.82; H, 7.01; N, 7.48		"
Dicinchonidine maleate	$(C_{19}H_{22}N_2O)_2C_4H_4O_4$	182°	C, 71.24; H, 7.13; N, 8.07		C, 71.59; H, 6.81; N, 7.95
Dicinchonidine fumarate	"	186	C, 71.31; H, 7.21; N, 8.18		"
Distrychnine maleate	$(C_{21}H_{23}N_2O_2)_2C_4H_4O_4 \cdot 2H_2O$	210°	C, 66.91; H, 6.62; N, 7.18; $H_2O$ , 4.15		C, 67.31; H, 6.34; N, 6.83; $H_2O$ , 4.39
Bistrychnine fumarate	$(C_{21}H_{23}N_2O_2)_2C_4H_4O_4 \cdot 4H_2O$	240°	C, 64.02; H, 6.88; N, 6.87; $H_2O$ , 8.12		C, 64.48; H, 6.54; N, 6.54; $H_2O$ , 8.1
Diquinidine maleate	$(C_{20}H_{23}N_2O_2)_2C_4H_4O_4$	98-99°	C, 68.67; H, 7.32; N, 7.67		C, 69.1; H, 6.8; N, 7.32
Diquinidine fumarate	"	154°	C, 68.82; H, 7.14; N, 7.45		"
Brucine mesaconate	$(C_{22}H_{25}N_2O_4)_2C_3H_4O_4 \cdot 5H_2O$	205-07°	C, 60.41; H, 6.85; N, 5.73; $H_2O$ , 8.5		C, 60.7; H, 6.74; N, 5.5; $H_2O$ , 8.9
Brucine citraconate	$(C_{22}H_{25}N_2O_4)_2C_3H_4O_4 \cdot 4H_2O$	209-10°	C, 61.34; H, 6.8; N, 5.97; $H_2O$ , 6.8		C, 61.8; H, 6.6; N, 5.65; $H_2O$ , 7.2

Disinchonidine mesaconate	$(C_{19}H_{23}N_3O)_2 \cdot C_4H_6O_4$	216-17°	C, 70°83; H, 7°14; N, 7°91	C, 70°86; H, 6°96; N, 7°79
Disinchonidine citraconate	"	173-75°	C, 70°56; H, 7°25; N, 8°14	"
Strychnine crotonate*	$(C_{21}H_{27}N_7O_3)_2 \cdot C_4H_6O_2$	215-17	C, 71°01; H, 6°79; N, 6°83	C, 71°42; H, 6°6; N, 6°6
Strychnine isocrotonate	"	250-52°	C, 70°87; H, 6°8; N, 6°98	"
Quinine crotonate	$(C_{20}H_{24}N_2O_2) \cdot C_4H_6O_2$	*136°	C, 69°9; H, 7°6; N, 7°08	C, 70°24; H, 7°31; N, 6°89
Quinine isocrotonate	"	*160-162°	C, 69°74; H, 7°41; N, 7°14	"
Distrychnine mesaconate	$(C_{21}H_{23}N_7O_3)_2 \cdot C_4H_6O_4$ $3H_2O$	230°	C, 65°87; H, 6°73; N, 6°69; H <sub>2</sub> O, 6.09	C, 66°1; H, 6°57; N, 6°57; H <sub>2</sub> O, 6°08
Distrychnine citraconate	$(C_{21}H_{23}N_7O_3)_2 \cdot C_4H_6O_4$ $3H_2O$	*185°	C, 67°39; H, 6°63; N, 6°9; H <sub>2</sub> O, 3°86	C, 67°62; H, 6°47; N, 6°71; H <sub>2</sub> O, 3°31
Diquinine mesaconate	$(C_{20}H_{24}N_2O_2)_2 \cdot C_4H_6O_4$	215-16°	C, 69°6; H, 7°03; N, 7°28	C, 69°41; H, 6°9; N, 7°19
Diquinine citraconate	"	*96-98°	C, 69°15; H, 7°2; N, 7°31	"

\* Refers to m. p. without decomposition, the rest melt with decomposition.

Temp. 31°.		TABLE II.				Diquinine fumarate							
Conc. per 100 c. c.		Actual rotation.		Specific rotation.		Molecular rotation.		Actual rotation.		Specific rotation.		Molecular rotation.	
0.9440 g.		2.474°		-131.08°		-1001.06°		2.398°		-127.09°		-960.9°	
0.4720		1.181		-125.10		-949.3		1.146		-121.39		-927.4	
0.2360		0.441		-93.43		-710.13		0.391		-82.83		-681.8	
0.1180		0.189		-80.08		-612.1		0.171		-72.45		-598.9	
Temp. 30°.		Dicinchonidine maleate				Dicinchonidine fumarate							
1.3312		2.816		-106.73		-744.3		2.642		-99.28		-698.57	
0.3328		0.663		-89.6		-701.18		0.609		-91.4		-643.4	
0.1664		0.335		-85.64		-603.9		0.264		-79.2		-558.5	
0.0832		0.134		-80.52		-584.3		0.123		-73.9		-520.5	
Temp. 24°.		Distrychnine maleate				Distrychnine fumarate							
1.084		0.912		-42.06		-344.5		0.846		-39.02		-834.01	
0.542		0.406		-37.18		-304.8		0.35		-32.28		-276.3	
0.271		0.187		-34.5		-282.9		0.16		-29.52		-252.6	
0.1365		0.086		-31.36		-257.15		0.069		-25.46		-217.9	



Temp. 30°.

*Diquinidine maleate**Diquinidine fumarate*

Conc. per 100 c. c.	Actual rotation.	Specific rotation.	Molecular rotation.	Actual rotation.	Specific rotation.	Molecular rotation.
1.2544 g.	5.27	210.06	1604.85	5.225	208.26	1591.1
0.6273	2.61	208.05	1589.5	2.582	205.8	1572.3
0.3136	1.28	204.08	1559.17	1.25	190.29	1522.5
Temp. 24°.						
			<i>Brucine citraconate</i>			<i>Brucine mesaconate</i>
1.6816	1.295	-38.5	-388.08	1.136	-33.78	-394.4
0.8408	0.585	-34.79	-1050.85	0.510	-30.32	-300.16
0.4204	0.240	-28.34	-285.66	0.217	-25.8	-255.42
Temp. 30°.						
			<i>Cinchonidine citraconate</i>			<i>Cinchonidine mesaconate</i>
2	3.95	-98.75	-709.02	3.66	-91.5	-656.9
1	1.75	-87.5	-628.25	1.65	-83.5	-592.35
0.8	1.304	-81.5	-585.17	0.608	-69.8	-501.16
0.5	0.75	-75	-538.5	0.402	-62.75	-488.44
0.4	0.541	-67.86	-485.79	0.215	-53.75	-385.92
0.2	0.239	-59.55	-429.7	1.27	-79.3	-569.37



Temp. 30°.

Conc. per 100 c. c.	<i>Diquinine citraconate</i>				<i>Diquinine mesaconate</i>			
	Actual rotation.	Specific rotation.	Molecular rotation.		Actual rotation.	Specific rotation.	Molecular rotation.	
1.252 g.	3.292	-131.4	-1022.20		3.195	-127.6	-992.72	
0.626	1.561	-124.69	-970.01		1.525	-121.8	-947.6	
0.313	0.7234	-115.5	-608.50		0.731	-105.5	-820.79	
0.1565	0.287	-91.7	-713.12		3.246	-84.98	-661.14	

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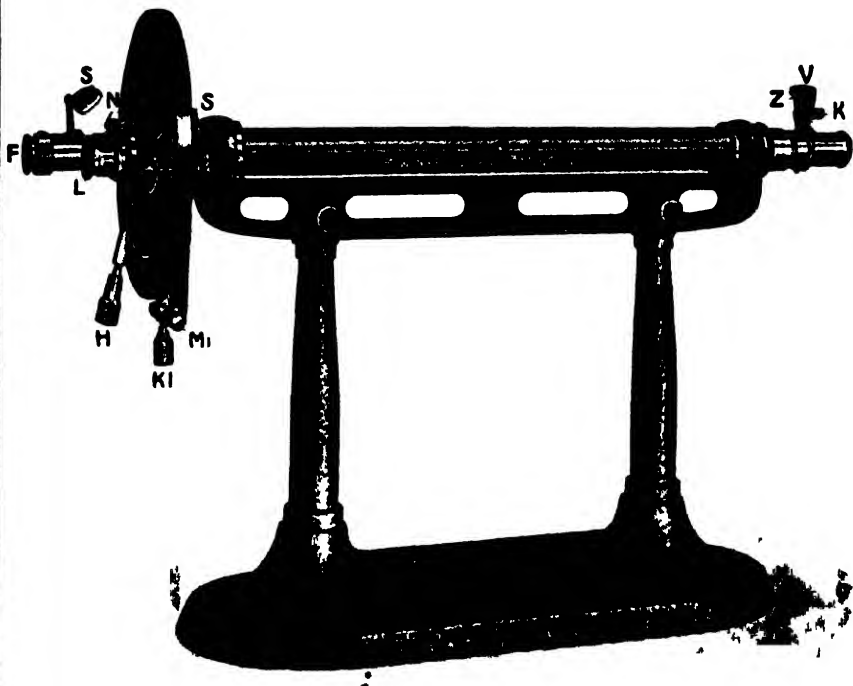
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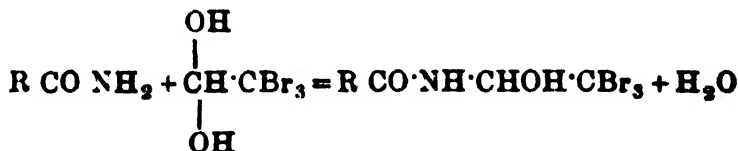
## Condensation of Bromal Hydrate with Aliphatic Amides.

BY B. H. YELBURG.

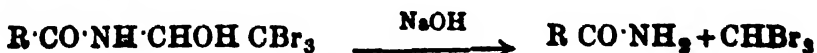
Although the chloral amide derivatives have been studied carefully, less work has been done on the corresponding compounds of bromalamides, inspite of their physiological importance. Bischoff prepared bromalurethane (*Ber.*, 1874, 7, 628) and Schiff and Tassinari bromalacetamide (*Ber.*, 1877, 10, 1786)

In the work here described, a series of aliphatic amides from formamide up to pelargonamide, have been condensed with bromal hydrate and the properties of the products have been compared with those of the corresponding chloral derivatives.

The bromalamides are obtained by mixing excess of bromal hydrate with the amide and heating until a solid is formed. The reaction proceeds as follows:—



Cold sodium hydroxide solution converts them into bromoform and the corresponding amide. The higher members of the series react more slowly.



The bromalamides differ from the chloralamides in some respects. They can be divided into two groups: (i) Formamide to butyramide, (ii) valeramide to pelargonamide.

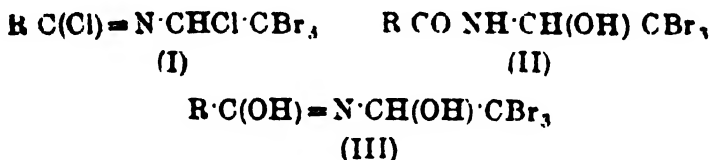
Compounds of the group (i) are more reactive and the reduction products less stable than those of the group (ii). The chloral compounds of the group (i) are more readily formed than those of the group (ii). Bromalformamide is obtained only with concentrated sulphuric acid as the condensing agent. With sodium hydroxide, the bromal compounds of the first group decompose more readily than those of the chloral compounds.

The presence of the OH group in the condensation products gives rise to a number of derivatives such as, acetyl, benzoyl, methoxy and anhydro.

*Action of acetic anhydride.*—By treating the condensation products with acetic anhydride in presence of concentrated sulphuric acid the acetyl derivatives are obtained, while in presence of dilute sodium hydroxide at 0°, the anhydro compounds are the main products provided the final mixture remains acidio. It has been found that the acetyl derivatives of the group (ii) viz., acetyl-, onanth-, capryl-, and pelargonamides are very easily prepared by Chattraway's method (*J. Chem. Soc.*, 1931, 2495).

*Action of dimethyl sulphate*—Owing to the unstability of the bromal compounds in presence of alkali, the methylation was carried out at 0° (*cf.* Feist, *Ber.*, 1912, **45**, 945); bromalformamide could not be methylated at all. Methylation takes place more readily with the compounds of the group (ii).

As the condensation products, when treated with two molecules of phosphorus pentachloride, give rise to the compounds of the type (I) they probably exist in tautomeric forms (II) and (III) (*cf.* Schiff and Tassinari, *loc. cit.*).



The constitution of the reduction products of the bromalamides has been discussed by Yelburgi and Wheeler in a paper communicated to this journal.

#### EXPERIMENTAL

*Bromal formamide.*—Formamide (8 g.) and bromal hydrate (58 g) were heated together till a clear solution was formed. It was cooled, mixed with a few drops of concentrated sulphuric acid, left for 2—3 days, poured over crushed ice and then kept in the refrigerator for about 6 hours. The product crystallised as tiny plates from methyl alcohol, m. p. 139-40°, yield 18 g. Unlike the other bromal amides, it is soluble in water. (Found: Br, 73.5.  $\text{C}_3\text{H}_4\text{O}_2\text{NBr}_3$  requires Br, 73.6 per cent).

The acetyl derivative, obtained in the usual manner, crystallised in needles, m. p. 107.8°. (Found: Br, 65.1.  $\text{C}_5\text{H}_6\text{O}_3\text{NBr}_3$  requires Br, 65.2 per cent).

The *benzoyl* derivative was obtained as needles, m. p.  $189^{\circ}$ . (Found: Br, 55.6.  $C_{10}H_8O_3NBr_3$  requires Br, 55.8 per cent).

*Anhydrodibromalformamide*.—Bromalformamide (3 g.) was dissolved in sodium hydroxide solution (1%, 50 c.c.), and acetic anhydride was added to it at  $0^{\circ}$  slowly with shaking until the mixture remained faintly acidic. The mixture was then left in the refrigerator overnight. It crystallised as thin plates from dilute alcohol, charring at  $160^{\circ}$  and melting at  $170^{\circ}$ . (Found: Br, 75.6.  $C_6H_8O_3N_2Br_6$  requires Br, 75.7 per cent). All the anhydro derivatives of the remaining bromalamides are similarly obtained.

*$\beta$ -Tribromo- $\alpha$ -chloroethylformamide*.—Bromalformamide (5 g.) was mixed with phosphorus pentachloride (2.9 g.) in a tube fitted with calcium chloride tube and heated until the evolution of hydrogen chloride slackened. The product was obtained as a colourless liquid, b.p.  $80^{\circ}/15$  mm. ( $C_3H_5ONClBr_3$  requires Halogen,  $80.0$ . Found: Halogen, 79.9 per cent). The other chloro compounds are similarly prepared.

*Methylbromalacetamide*.—Bromalacetamide (5 g.) was dissolved in sodium hydroxide solution (1%, 50 c.c.), and excess of dimethyl sulphate (6.8 g.) was slowly added in the cold. The final mixture should remain fairly alkaline. The oily matter separating solidified on keeping in the refrigerator for 12 hours. It was obtained as thick plates from methylated spirit, m. p.  $106^{\circ}$ . (Found: Br, 67.8.  $C_5H_8O_2NBr_3$  requires Br, 67.8 per cent). The other methoxy derivatives are obtained similarly.

*$\beta$ -Dibromoethylneacetamide*.—As bromalacetamide when reduced with zinc dust and glacial acetic acid decomposed, its acetyl derivative was reduced. After reduction was complete, the mixture was filtered and the filtrate, after neutralisation with sodium carbonate paste at  $0^{\circ}$ , gave a solid. It was obtained as long rectangular plates from petroleum ether, m. p.  $82^{\circ}$ , yield 1 g. from 15 g. of acetyl bromalacetamide. (Found: Br, 65.5.  $C_4H_8ONBr_2$  requires Br, 65.8 per cent).

All the corresponding derivatives of the bromalamides are obtained similarly and possess similar properties. The reduction products of the group (i) are less stable than those of the group (ii) and the yield increases as we ascend the series.

*$\beta$ -Bromoethylneisovaleramide*.—Bromalisovaleramide (15 g.) was dissolved in glacial acetic acid (150 c.c.) and zinc dust (about 6 g.) was added to it in portions. After each addition of zinc dust

the reduction mixture must be cooled. The mixture was shaken for about 4 hours, filtered and the filtrate was mixed with crushed ice and neutralised with sodium carbonate paste at 0°. On keeping the neutral mixture in the refrigerator overnight, a solid separated which was filtered at once and kept on a porous plate and purified in the refrigerator. The product is unstable at ordinary temperature but remains unchanged for a number of days in the refrigerator, Long needles, m p. 71-74°. (Found: Br, 38·9  $C_7H_{12}ONBr$  requires. Br, 38·8 per cent).

The corresponding reduction products of the higher bromalamides are obtained in a similar way and have similar properties. The other new compounds prepared are summarised in the Tables.

TABLE I.

Name.	Formula.	Appearance.	M. p. or b. p.	Analyses. Found.	Calc.
Benzylbromalacetamide	$C_{11}H_{15}O_2NBr_3$	Needles	122°	Br, 53.9%	54.1%
Amylobromalacetamide	$C_9H_{13}O_2N_2Br_6$	Silky needles	183.85°	73.3	72.5
$\beta$ -Tribromo- $\alpha$ -chloroethyl- acetamide	$C_4H_6ONClBr_3$	Colourless liquid	76°/8 mm.	Halogen, 76.8	76.8
$\beta$ -Tribromo- $\alpha$ -chloroethyl- acetchlorimide	$C_4H_4NCl_2Br_3$	Colourless liquid	138°-25 mm	.. 82.2	82.5
Bromalpropionamide	$C_5H_7O_2NBr_3$	Rectangular plates	174°	Br, 67.7	67.8
Acetyl bromalpropionamide	$C_7H_9O_3NBr_3$	Plates	96.96°	60.3	60.6
Benzyl bromalpropionamide	$C_{13}H_{17}O_2NBr_3$	Plates	113.15°	53.3	52.4
Methylbromalpropionamide	$C_6H_9O_2NBr_3$	Thick plates	85.87°	65.1	65.2
Amylobromalpropionamide	$C_{11}H_{15}O_2N_2Br_3$	Silky needles	192°	62.3	62.5
$\beta$ -Tribromo- $\alpha$ -chloroethyl- propionamide	$C_5H_7ONClBr_3$	Colourless liquid	120°/19 mm.	Halogen, 73.7	73.9
Acetyl bromalbutyramide	$C_9H_{13}O_3NBr_3$	Thin plates	98.98°	Br, 58.5	58.6
Benzyl bromalbutyramide	$C_{13}H_{17}O_3NBr_3$	Thin plates	192°	• 50.6	50.8
Methyl bromalbutyramide	$C_7H_{11}O_3NBr_3$	Short needles	101°	62.7	62.6

TABLE I (contd.).

Name.	Formula	Appearance.	M.p. or b.p.	Found.	Analysis.	Calc.
Anhydrodibromalbutyramide	$C_{10}H_{16}O_3N_2Br_2$	Silky needles	155°	Br, 66.8%		66.8%
* <i>o</i> -Tribromo- <i>o</i> -chloroethylbutyramide						
Bromalisoobutyramide	$C_6H_9ONClBr_3$	Colourless liquid	126°/15 mm.	Halogen, 71.2		71.3
Acetyl bromalisoobutyramide	$C_8H_{10}O_3NBr_3$	Shining plates	156°	Br, 65.3		65.2
Benzoyl bromalisoobutyramide	$C_9H_{12}O_3NBr_3$	Shining tufts	141-43°	58.6		58.5
Benzoyl bromalisoobutyramide	$C_{12}H_{16}O_3N_2Br_3$	Shining tufts	131-32°	50.6		50.8
Methyl bromalisoobutyramide	$C_7H_{12}O_3NBr_3$	Needles	135°	62.6		62.8
Anhydrodibromalisoobutyramide	$C_{13}H_{18}O_3N_2Br_2$	Silky needles	155°	66.7		66.8
Bromalisovaleramide	$C_7H_{12}O_3NBr_3$	Sparkling plates	149°	62.7		62.8
Acetyl bromalisovaleramide	$C_9H_{14}O_3NBr_3$	Shining tufts	110-42°	56.5		56.6
Benzoyl bromalisovaleramide	$C_{14}H_{18}O_3NBr_3$	Shining tufts	98-100°	49.2		49.4
Methyl bromalisovaleramide	$C_6H_{10}O_3NBr_3$	Long rectangular plates	115-17°	60.5		60.6
Anhydrodibromalisovaleramide	$C_{11}H_{16}O_3N_2Br_2$	Shining needles	131-32°	64.1		64.3
Benzoyl isopropionamide	$C_8H_{11}O_3NBr_3$	Thin shining plates	116°	60.5		60.6
Acetyl bromalisoopropionamide	$C_{10}H_{16}O_3NBr_3$	Shining tufts	131-22°	54.7		54.8



Benzoylbromalcapronamide	$C_{15}H_{19}O_3NBr_3$	Thin plates	182-34°	Br, 47°	48°0
Methylbromalcapronamide	$C_{14}H_{18}O_3NBr_3$	Long rectangular plates*	105-07	58°6	58°5
Anhydrodibromalcapronamide	$C_{14}H_{16}O_3N_2Br_4$	Silky needles	155°	61°8	62°0
*Bromal-oxanthamide	$C_9H_{10}O_3NBr_3$	Thin shining plates	142°	58°4	58°5
Acetyl bromaloxanthamide	$C_{11}H_{12}O_3NBr_3$	Shining needles	135-36°	53°0	53°1
Benzoylbromaloxanthamide	$C_{15}H_{18}O_3NBr_3$	Thin plates	126°	46°5	46°7
Methylbromaloxanthamide	$C_{14}H_{16}O_3NBr_3$	Long rectangular plates	164-95	56°6	56°6
Bromalcaprylamide	$C_{14}H_{18}O_3NBr_3$	Shining thin plates	130°	56°4	56°6
Acetyl bromalcaprylamide	$C_{13}H_{16}O_3NBr_3$	Silky needles	129°	51°4	51°5
Benzoylbromalcaprylamide	$C_{17}H_{22}O_3NBr_3$	Shining tufts	108-10°	45°3	45°5
Methylbromalcaprylamide	$C_{11}H_{16}O_3NBr_3$	Long plates	45	54°6	54°8
Anhydrodibromalcaprylamide	$C_{13}H_{14}O_3N_2Br_4$	Silky needles	164°	57°8	57°8
*Bromalpelargonamide	$C_{11}H_{12}O_3NBr_3$	Shining thin plates	139°	54°6	54°8
Acetyl bromalpelargonamide	$C_{13}H_{14}O_3NBr_3$	Silky needles	131°	50°2	50°0
Benzoylbromalpelargonamide	$C_{15}H_{16}O_3NBr_3$	Shining tufts	123-26°	44°1	44°3
Methylbromalpelargonamide	$C_{13}H_{16}O_3NBr_3$	Needles	72-74°	53°0	53°1

\* The anhydro-derivative could not be prepared owing to the formation of a thick paste.

TABLE II.

Name.	Formula.	Appearance.	M. p.	Found.	Calc.
<i>p</i> -Dibromoethylencapronamide	$C_8H_7ONBr_2$	Long rectangular plates	84–86°	Br, 61.9%	62.9%
<i>p</i> -Dibromoethylencapronamide	$C_8H_7ONBr_2$	Fine needles	78–80°	58.8	59.0
<i>p</i> -Dibromoethylencapronamide	$C_8H_7ONBr_2$	Plates	80–83°	58.7	59.0
				C, 26.3; H, 3.4	C, 26.5; H, 3.4
<i>p</i> -Dibromoethylencapronamide	$C_8H_7ONBr_2$	Needles	68–70°	Br, 56.0	56.1
<i>p</i> -Dibromoethylencapronamide	$C_8H_7ONBr_2$	Long needles	74–75°	53.2	53.6
<i>p</i> -Dibromoethylencapronamide	$C_8H_7ONBr_2$	Shining needles	61–63°	36.2	36.4
Both the reduction products of onanthamide could not be prepared owing to the decomposition of the products.					
<i>p</i> -Dibromoethylencaprylamide	$C_{10}H_{11}ONBr_2$	Tufts	115°	48.9	48.9
<i>p</i> -Bromoethylencaprylamide	$C_{10}H_{13}ONBr$	Shining needles	67–71°	31.9	32.3
<i>p</i> -Dibromoethylencaprylamide	$C_{10}H_{13}ONBr_2$	Shining tufts	63–64°	46.9	46.9
<i>p</i> -Bromoethylencaprylamide	$C_{11}H_{15}ONBr$	Colourless liquid	b. p. 148°/10 m.m.	30.2	30.5

The author expresses his thanks to Dr. T. S. Wheeler, Principal, Royal Institute of Science, Bombay, for his interest in this work.

ORGANIC CHEMISTRY DEPARTMENT,  
THE ROYAL INSTITUTE OF SCIENCE,  
BOMBAY.

Received January 21, 1933.

## Condensation of Ethyl Propylacetoacetate with Aromatic Amines. Part II.

By G. V. JADHAV

The work described in Part I (*J. Indian Chem. Soc.*, 1931, 8, 681) has now been extended to  $\alpha$ - and  $\beta$ -naphthylamines, *o*-phenetidine, *m*- and *p*-aminophenols, *m*- and *p*-nitroanilines and *o*-, *m*- and *p*-chloroanilines.

Except with *m*-aminophenol, substituted carbamides  $\text{CO}(\text{NHR})_2$  are obtained in addition to the simple anilide  $\text{CH}_3\text{CO} \cdot \text{CH}(\text{C}_2\text{H}_5) \cdot \text{CO}(\text{NHR})$ ; but with  $\alpha$ -naphthylamine the amide cannot be isolated. The carbamides are always formed and the yield increases with the time of heating the reaction mixture.

The constitution of the carbamide derivatives was confirmed by preparing them according to the method of Mistry and Guha (*J. Indian Chem. Soc.*, 1930, 7, 793) by boiling urea with the corresponding amine in amyl alcoholic solution and finding the mixed melting points, when no lowering was observed.

The constitution of the carbamides from  $\alpha$ -naphthylamine, *o*-phenetidine, *m*- and *p*-nitroanilines and *o*-, *m*-, and *p*-chloroanilines was further confirmed by heating the compounds with acetic anhydride and fused sodium acetate when the corresponding acetyl derivatives were obtained. The mixed melting points with specimens prepared from the amines and acetic anhydride showed no lowering; *p*-aminophenol gave the diacetyl derivative.

### EXPERIMENTAL

***Di- $\alpha$ -naphthylcarbamide.***—A mixture of  $\alpha$ -naphthylamine (4 g.) and ethyl propylacetoacetate (5 g.) was boiled for about 10 minutes. The solid separating on cooling was washed with benzene and crystallised from glacial acetic acid in white needles,  $\mu$  p 296°. (Found: N, 8.77.  $\text{C}_{21}\text{H}_{16}\text{ON}_2$  requires N, 8.97 per cent.)

The melting point of  $\alpha\alpha'$ -dinaphthylcarbamide, described in literature, is indefinite.\*

\* It melts at 273° (Delbos, *Annales*, 1847 84, 370; Zinnin, *ibid.*, 1859, 100, 296; Pegliani, *Ber.*, 1879, 12, 385; Huhn, *Ber.*, 1885, 18, 2405) at 284-86° (Young and Clark, *J. Chem. Soc.*, 1897, 71, 1901), at 314-15° (Vittanet, *Bull. Soc. chim.*, 1874, ii, 21, 950), at 295-96° (Walther and Widkowski, *J. pr. Chem.*, 1898, 59, 278; Guha and Saksure, *J. Indian Chem. Soc.*, 1929, 6, 574; Mistry and Guha, *loc. cit.*)

**Di- $\beta$ -naphthylcarbamide.**—It was prepared and crystallised in the same way as the  $\alpha$ - compound, m. p.  $810^{\circ}$ .† (Found : N, 8.66.  $C_{21}H_{16}ON_2$  requires N, 8.97 per cent).

**n-Propylacetoacet- $\beta$ -naphthylamide.**—The benzene filtrate from di- $\beta$ -naphthylcarbamide preparation was evaporated, the solid washed with petroleum ether and repeatedly crystallised from alcohol, m.p.  $115-16^{\circ}$  (Found : N, 5.52.  $C_{17}H_{15}O_2N$  requires N, 5.20 per cent).

The same procedure was followed in subsequent preparations, the ester and the respective amine being taken in molecular proportions. The carbamide derivatives, being insoluble in benzene, could be separated from the soluble anilides.

**o-Diethoxydiphenylcarbamide**, obtained from o-phenetidine and the ester, was crystallised from boiling glacial acetic acid in white needles, m. p.  $220-21^{\circ}$ . (Found : N, 9.68.  $C_{17}H_{20}O_3N_2$  requires N, 9.88 per cent). Migliacci and Gargiulo (*Gazzetta*, 1928, 58, 110) records the melting point as  $222^{\circ}$ .

**n-Propylacetoacet-o-phenetidine.**—The benzene filtrate from the above experiment was evaporated and the residue was washed with petroleum ether. It is soluble in ethyl alcohol and dilute acetic acid. It crystallised from methyl alcohol in white needles, m.p.  $90-91^{\circ}$ . (Found : N, 5.6.  $C_{15}H_{21}O_3N$  requires N, 5.32 per cent).

**p-Dihydroxydiphenylcarbamide**, obtained from p-aminophenol and the ester, was triturated with dilute hydrochloric acid to remove the unacted phenol and crystallised from glacial acetic acid. It shrinks at  $270^{\circ}$  and melts at  $280^{\circ}$  (decomp.). Struve and Radenhousen (*J. pr. Chem.*, 1895, ii, 52, 238) record its m. p.  $230^{\circ}$  and Mistry and Guha (*loc. cit.*),  $288^{\circ}$  (decomp.) (Found : N, 11.5.  $C_{13}H_{13}O_3N_2$  requires N, 11.48 per cent).

**n-Propylacetoacet-p-hydroxyphenylamide.**—The filtrate from the above experiment on evaporation, gave a thick oily liquid with some solid. The oil was drained off and the solid was dried on a porous plate for several days. It is very soluble in almost all organic solvents. It was finally crystallised from dilute alcohol, m. p.  $95-96^{\circ}$ . (Found : N, 6.83.  $C_{13}H_{17}O_3N$  requires N, 5.96 per cent).

**n-Propylacetoacet m-hydroxyphenylamide.**—m-Aminophenol (5 g.) and the ester (8 g.) were refluxed for about 1 hour. On cooling the liquid became a thick paste from which solid separated on treating

† The melting point of  $\beta\beta$ -dinaphthylurea is recorded as  $293^{\circ}$  (Hahn, *loc. cit.*);  $300^{\circ}$  (Walther and Widkowski, *loc. cit.*);  $290^{\circ}-90^{\circ}$  (Yonng, *J. pr. Chem.*, 1899, 69, 255);  $300-10^{\circ}$  (Vittenot, *loc. cit.*; Guha and Saksore, *loc. cit.*; Mistry and Guha, *loc. cit.*) and  $298^{\circ}$  (Ekstrand, *Ber.*, 1887, 20, 1550).

with a mixture of benzene and little ether. It was first washed with benzene and finally with dilute hydrochloric acid to remove the unacted phenol and finally crystallised from dilute acetic acid (1:1) in needles, m. p. 223-24°. (Found: N, 6.28.  $C_{13}H_{17}O_3N$  requires N, 5.96 per cent)

The *acetyl* derivative, prepared in the usual manner, crystallised from dilute alcohol in needles. It shrinks at 150° and completely melts at 165° (Found: N, 5.39.  $C_{15}H_{19}O_4N$  requires N, 5.05 per cent).

*o*-Dichlorodiphenylcarbamide, obtained from *o*-chloroaniline and the ester was crystallised from glacial acetic acid in colourless needles, m. p. 235-36°. It is soluble in methyl and ethyl alcohols and acetic acid, insoluble in benzene, ether, chloroform, carbon tetrachloride and petroleum ether (Found N, 9.68; Cl, 25.54  $C_{13}H_{10}ON_2Cl_2$  requires N, 9.97, Cl, 25.27 per cent) Vittenet (*Bull. Soc. chim.*, 1899, *iii*, 21, 303) gives the m. p. 235-36° and Manuelli and Rosellini (*Gazzetta*, 1899, 29 *n*. 128) 238°

*n*-Propylacetoacet *o*-chloroanilide.—The filtrate from the above experiment was evaporated, the residue washed with petroleum ether and crystallised from dilute methyl alcohol, m. p. 83-84°. It is easily soluble in most of the common organic solvents. (Found: N, 5.32; Cl, 13.59  $C_{15}H_{16}O_2NCl$  requires N, 5.52; Cl, 14.0 per cent).

The same compound was obtained by heating the reaction mixture at 140-50° for about 10 hours

*m*-Dichlorodiphenylcarbamide was prepared in the same way as its *ortho* isomer and crystallised from glacial acetic acid in colourless needles, m. p. 245-46° \* It resembles the *ortho* compound in its solubility. (Found: N, 9.68; Cl, 25.35  $C_{13}H_{10}ON_2Cl_2$  requires N, 9.97; Cl, 25.27 per cent).

*n*-Propylacetoacet-*m*-chloroanilide was isolated from the benzene filtrate as in the case of its *ortho* isomer and crystallised from dilute alcohol, m. p. 88-89°. It resembles the *ortho* compound in solubility. (Found: N, 5.80; Cl, 13.89  $C_{15}H_{16}O_2NCl$  requires N, 5.52; Cl, 14.0 per cent) It can also be prepared by heating the reaction mixture at 140-50° for about 6 hours

*p*-Dichlorodiphenylcarbamide was prepared in the same way as the *ortho* isomers but heating was required for only 45 minutes. It

\* It melts at 245° (Vittenet, *Bull. Soc. chim.*, 1899, *iii*, 21, 303), at 245°. (Manuelli and Rosellini, *loc. cit.*; Struve and Radenhausen, *J. pr. Chem.*, 1901, 66, *ii*, 329).

crystallised from glacial acetic acid in white needles, m. p. 289-90°.\* (Found: N, 9.72; Cl, 24.97.  $C_{13}H_{10}ON_2Cl_2$  requires N, 9.97 Cl, 25.27 per cent).

*n*-Propylacetoacet-*p*-chloroanilide was obtained from the benzene filtrate like its isomers and crystallised from alcohol, m. p. 123-24°. (Found: N, 5.70; Cl, 13.72.  $C_{13}H_{10}O_2NCl$  requires N, 5.52; Cl, 14.0 per cent). It can be prepared by heating the reaction mixture at 140-50° for 6 hours.

*m*-Dinitrodiphenylcarbamide obtained from *m* nitroaniline and the ester was crystallised from glacial acetic acid in straw yellow needles, m. p. 241-42°.† (Found: N, 18.75.  $C_{13}H_{10}O_5N_4$  requires N, 18.55 per cent).

*n*-Propylacetoacet-*m*-nitroanilide.—The filtrate from the above experiment on evaporation gave a solid which was first washed with petroleum ether and then with dilute hydrochloric acid and crystallised from dilute acetic acid, m. p. 95-96° (Found: N, 10.51.  $C_{13}H_{10}O_4N_2$  requires N, 10.61 per cent). The compound can be obtained by heating the reaction mixture at 170-80° for 4 hours.

*p*-Dinitrodiphenylcarbamide was prepared in the same way as its *meta* isomer, m. p. 310°; (Found: N, 18.71.  $C_{13}H_{10}O_5N_4$  requires N, 18.55 per cent).

*n*-Propylacetoacet-*p* nitroanilide was obtained from the benzene filtrate in the same way as its *meta* isomer and crystallised from acetic acid, m. p. 118-19°. (Found N, 10.64.  $C_{13}H_{10}O_4N_2$  requires N, 10.61 per cent).

\* It melts at 270° (Beilstein and Kurbatow *Invalen* 1875, 176, 51), at 306-07° (Vittenet, *loc cit* at 275° (Manuelli and Rosellini *loc cit*) at 310° (Chattaway and Orton *Ber* 1901, 34, 1075, Bamberger and Destrez, *Ber* 1902, 35, 1878), at 270° (Bougault and Lebourg, *Bull. Soc. chim.*, 1930, 47, 594).

† It melts at 233° (Losanitsch, *Ber.*, 1843, 18, 50), at 227° (Struve and Radenhausen, *J. pr. Chem.*, 1895, 11, 82, 213) at 225° Vittenet, *Bull. Soc. chim.*, 1899, 11, 21, 156; Offret, *ibid.*, p. 778; Manuelli and Rosellini (*loc cit*), at 223° (Loh and Dehn, *J. Amer. Chem. Soc.*, 1926, 48, 2956).

‡ The melting point of this compound has been recorded as 312 (Struve and Radenhausen, *J. pr. Chem.*, 1895, 11, 82, 238; Manuelli and Rosellini, *loc cit*) and 310° (Vittenet, *Bull. Soc. chim.*, 1899, 11, 21, 149; Mistry and Guba, *loc cit*).

## **The Fat and the Oil from the Seeds of *Actinodaphne Hookeri*, Meissn. An Indigenous Source of Lauric Acid.**

BY S. V. PUNTAMBEKAR AND S. KRISHNA.

During the investigation on the alkaloid from the bark of *Actinodaphne* (Krishna and Ghose, *J. Indian Chem. Soc.*, 1932, **9**, 429) the seeds were examined for their alkaloidal content. No alkaloid, however, was found in them but only a small quantity (1%) of an essential oil which appeared in its characteristics to be similar to the oil of *Litsa zeylanica* (Rao, *J. Ind. Inst. Sci.*, 1932, **15A**, 72) which like *Actinodaphne Hookeri* belongs to the N. O. Laurinaceae. Apart from the essential oil, the seeds contained a large quantity of a fat and an oil which has been described by Kirtikar and Basu ('*Indian Medicinal Plants*,' Pt. II, p. 1103) as 'Pisitela' employed medicinally as an external application to sprains. Of the species of the N. O. Laurinaceae occurring in India, only the fats from the seeds of *Litsa sebifera* and *L. zeylanica* appear to have been studied (Schroeder, *Arch. Pharm.*, 1905, **243**, 631; Hooper, *Annual Report, Indian Museum*, 1910 p. 10) and in order to collect additional information it was thought desirable to investigate the composition of the fat from *Actinodaphne Hookeri*.

The results obtained show that the kernels contain a fat which consists mainly of trilaurin (96%) and endocarp contains an oil which consists mainly of the glycerides of oleic acid but the fat as extracted is never obtained in pure form and is always found to contain small quantities of triolein. In actual practice, it is not possible to separate the seed-shells (endocarp) from the kernels or the kernels from the endocarp very completely with the result that some of the oil from the endocarp gets mixed with the fat and *vice versa*. The fat, which is hard and slightly coloured, can very easily be purified, a single crystallisation from alcohol giving pure trilaurin of iodine value 1.

Not many examples are known where a fat from natural sources has been found to consist of a glyceride of a single fatty acid and, therefore, the investigation is of further interest from an academic point of view. It has also a commercial interest in that the fat could be employed as an indigenous source of lauric acid.

*The Kernel Fat.*

The *actinodaphne* seeds used in this investigation were obtained from Mahabaleshwar (Bombay Presidency). The kernels were separated from the endocarp, powdered and extracted with petroleum ether when contain 75% of a fat (or 48.4% of the original seeds) was obtained. For determination of the physical and chemical constants, the powdered kernels were expressed at about 50° in a hydraulic press and in this manner only 48% (or 31% of the seeds) of a pale yellow oil was obtained which on standing became hard and crystalline.

*General characteristics.*

Consistency	..	Hard, brittle and crystalline
Colour	..	Pale yellow
M.p.	..	43-44°
Sp. gr.	...	0.925 at 25°
Refractive index	...	1.4480 at 30°
Saponification value	..	255.5
Iodine value (Hanus)	.	10.9
Acetyl value	..	11.3
Hehner value	...	91.0
Acid value	..	4.0
Unsaponifiable matter	.	1.02%

*Composition of the fatty acids.*—The fat, when crystallised from a large volume of alcohol, was obtained in fine silky needles, m.p. 45-46°, saponification value 264, and iodine value 1.2. The fat when saponified gave an acid which on crystallisation from dilute alcohol melted at 43-44° and had M.W. 200.5. Its melting point when mixed with an authentic sample of lauric acid remained unchanged. These facts indicated that the fat was almost entirely trilaurin.

For the determination of the composition of the fat, as much as possible of the sparingly soluble trilaurin of iodine value 0, was removed by crystallisation of the fat from 95% alcohol and the residue left in the mother liquor was then saponified and separated into solid and liquid acids by the Twitchell's method. Identification of the acids was conducted as described later.

*Chemical constants of the mixed fatty acids.*

Mean molecular weight	...	202
Iodine value (Hanus)	...	3.15
Saturated acids	...	96%
Unsaturated acids	...	4%



*Unsaturated acids.*—100 G. of the fat were crystallised from boiling 95 % alcohol (1 litre) and in this way a snow white, silky, needle shaped crystalline product (90 g.) of m.p. 45–46° and saponification value 264, was obtained which was identified as trilaurin. The residual 10 g. of the fat remaining in the mother liquor was saponified with alcoholic potash and the acids liberated. The fatty acids (9.5 g.) thus isolated were further separated into solid and liquid acids by the lead salt—alcohol method and in this manner the following two fractions were obtained: Fraction A—liquid acids (5.8 g.) of iodine value 61.7, and Fraction B—solid acids (3.7 g.) of iodine value 3.2.

A portion of the liquid acids on bromination did not yield any hexabromide nor could any tetrabromide be isolated from the brominated product. Another portion of (A) was converted into its potassium soap and oxidised in the cold by a dilute solution of potassium permanganate according to the method of Lapworth and Mottram (*J. Chem. Soc.*, 1925, 127, 1628). The oxidised product, after removal of the unoxidised portion with petroleum ether and after being twice crystallised from alcohol, melted at 120–30° and had a M. W. of 318 and was identified as dihydroxystearic acid. The unoxidised portion was left as a pasty brown mass which on washing with dilute alcohol and drying was found to have a M. W. of 210. These experiments indicated that the unsaturated acids in the portion (A) consisted mainly of oleic acid and that the acids of more than one double bond, namely, linoleic and linolenic etc., were absent. They also indicated that portions (A) and (B) still contained some solid acid most of which was lauric. The amount of liquid acids being small, their conversion into methyl esters and subsequent fractionation was not attempted.

*Saturated acids.*—The solid acids (B), on twice crystallisation from dilute alcohol, melted at 43–44° and had M. W. of 200.5. Its melting point showed no depression when mixed with an authentic sample of pure lauric acid. The fatty acids, (B), therefore, consisted mainly of lauric acid with a little oleic acid as indicated by their iodine value.

In order to prepare the methyl ester 825 g. of the mixed acids, from which the unsaponifiable matter had been removed, was successively crystallised from 75 % alcohol to remove oleic acid as completely as possible, and 154 g. of an acid (m. p. 44°; M. W. 200.7 and iodine value 1.6) was isolated. This was converted into its

methyl ester which distilled at 132-35°/7 mm. and only a small portion (iodine value 4) distilled at 185-160° and this appeared to be a mixture of lauric and oleic esters. The fraction boiling at 132-35° had a saponification equivalent of 214 and the acid liberated from this melted at 43-44° and was identified as lauric acid. The above data on calculation gave the following percentage composition for the mixed acids namely, lauric (96 %) and oleic 4 %).

#### *The Endocarp Oil.*

The seed-shells on extraction with petroleum ether gave 25% (8.75 % of the seeds) of a reddish brown oil which on cooling to 20° deposited a solid crystalline matter, subsequently identified as trilaurin. The oil on removal of the solvent and the solid matter was cooled to 0° and filtered rapidly under suction, when a further quantity of trilaurin was removed. The filtrate was used for determining the general characteristics which are as given below.

Consistency	...	..	Liquid
Colour	...	...	Reddish brown
Sp. gr.	..	...	0.9163 at 20
Refractive index	...	..	1.4570 at 25
Saponification value		..	199.6
Iodine value (Hanus)	..	..	51.6
Acetyl value	...	...	77.0
Acid value	..	...	160.2
Hebner value	..	...	181.0
Unsaponifiable matter	..	...	3.56 %

50.5 G. of the oil was saponified in the usual manner and extracted with ether to remove the unsaponifiable matter after which the mixed acids gave the following chemical constants.

Mean molecular weight	..	...	..	265
Iodine value (Hanus)	...	...	...	51.6
Resin acids	..	...	...	11.2 %
Saturated fatty acids	...	...	...	33.0 %
Unsaturated fatty acids	..	...	...	55.6 %

36 G. of the acids from which the unsaponifiable matter had been removed was subjected to the usual Twitchell's separation with the following results.

A—Acids whose lead salts were insoluble in boiling 95% alcohol in the presence of acetic acid (mostly resin acids)			
	...	...	.. 4.04 g
B—Saturated fatty acids	...	...	.. 2.42 g.
C—Unsaturated fatty acids	...	...	.. 29.80 g

Total    36.00

The acids (A) (M. W. 819; iodine value 18), consisted mainly of resin acid and no definite product could be isolated by crystallisation.

The acids (B) (M.W. 243; iodine value 3.2), on being dissolved in petroleum ether deposited a small amount of resinous matter. The residues from the ethereal filtrate on crystallisation from acetone melted at 48° and had a M. W. of 249. The residue from this on crystallisation from alcohol gave a substance (m.p. 44-45°; M. W. 208). The acids (B), therefore, appear to be a mixture of resin and lauric acids.

The acids (C) (M. W. 208 and iodine value 51.5) were converted into their methyl esters in the usual manner and 28.4 g. of the neutral esters distilled at 2—3 mm. with the following results.

Fraction	B.p.	Weight	Iodine value.	Component of the esters		
				Methyl laurate	Methyl oleate or isomers	Isomeric methyl dihydroxystearate.
L <sub>1</sub>	107-12	1.95 g	4.6	1.85	0.10 g.	
L <sub>2</sub>	112-17	0.08	5.7	5.46	0.62	
L <sub>3</sub>	132-65°	1.57	31.7	0.99	0.58	
L <sub>4</sub>	165-70°	3.48	68.5	0.70	2.78	
L <sub>5</sub>	170-75°	9.20	81.0	0.00	9.20	
L <sub>6</sub>	175-200°	3.23	88.8		2.21	1.02 g.
Residue		2.70	41.3		1.30	1.40
Loss		0.19	...			
Total		28.40	.	9.03	16.79	2.42

Fractions L<sub>1</sub> and L<sub>2</sub> were mostly methyl laurate, saponification value 213.7 (saponification value for pure methyl laurate being 214) and the liberated acid from the product of saponification was identified as lauric acid. The presence of a little methyl oleate was indicated from its low iodine value.

Fractions L<sub>3</sub> and L<sub>4</sub> appeared to be mixtures of methyl oleate and methyl laurate.

Fraction L<sub>5</sub> was almost entirely methyl oleate, saponification value 800 (pure methyl oleate has a saponification value of 296 and iodine value 85.8).

Fraction L<sub>6</sub> on standing deposited some solid matter (m.p. 65°) which appeared to be the methylester of isomeric dihydroxystearic acid (cf. Puntambekar and Krishna, *J. Indian Chem. Soc.*, 1933, 10, 209).\*

\* In this paper (pp. 203-212) the following changes are to be read: Isomeric oleic acid for elaidic (isoleic) methyl oleate and isomers for methyl elaidic and oleate. Insert (isomeric) before dihydroxystearic acid (in the heading of the last column of the table, p. 210). The value 1.16% (p. 211, last column of the table) works out to be 3.35%, if instead of myristic acid the presence of palmitic acid is:

The residue was a dark brown viscous mass and appeared to be a mixture of methyl oleate and isomeric methyl dihydroxystearate and the decomposition products.

The above data on calculation gave the following percentage composition for the mixed acids. The mean molecular weight of the resin acids has been taken as 346 (Twitchell, *J. Soc. Chem. Ind.* 1891, 10, 805).

Acids.	Weight	Per cent
Resin	4.03 g	11.20
Lauric	11.88	33.00
Oleic and its isomers	17.56	48.74
Isomeric dihydroxystearic	2.53	7.02
Total	36.00	100.00

*Unsaponifiable matter from the fat and the oil* —The unsaponifiable matter from the fat was dissolved in hot alcohol and the solution allowed to cool. A flocculent amorphous matter separated out, which on drying melted at 60-70° and appeared to be wax. After removal of this substance the alcoholic solution yielded a phytosterol which after three crystallisations from alcohol melted at 130-31°. Its acetyl derivative melted at 118-19°. This shows that the sterol is sitosterol commonly found in vegetable oils and fats.

The amount of the unsaponifiable matter from the endocarp oil being small in quantity was not investigated further. In appearance and consistency it appeared very much like the unsaponifiable matter from the kernel fat.

#### SUMMARY.

1. The fat and the oil from the seeds of *Actinodaphne hookeri* are found to contain the glycerides of lauric, oleic, isomeric oleic acids together with sitosterol.
2. The oil contains a small amount of resin acids.
3. The fat appears to be a convenient source for lauric acid.

## **The Oil from the Seeds of *Tectona Grandis* (Teak).**

By S. V. PUNTAMBEKAR AND S. KRISHNA.

It is commonly stated in works on Indian Forestry that teak wood contains an oil to which is due its immunity to insect attacks. In some of the books it is stated that the quantity of this oil is so large that it could be used as a substitute for linseed oil. Gamble, for instance, writes that "teak wood is strongly and characteristically scented and containing an oil which is easily perceptible to the touch and is preservative" ("Manual of Indian Timbers", 1922, p. 526). "When quite fresh, teak hardly floats, but when seasoned it floats easily and the oil in the wood prevents its getting water-logged" (*ibid.*, p. 531). He further states that "the durability is probably due to the large amount of oil contained in the wood. This oil is used medicinally as a substitute for linseed oil and as a varnish, but it would seem that its extraction as an oil is difficult, but as a tar comparatively easy" (p. 532). Similar observations have been made by other writers. Vanstone ("Indian Woods in the Raw Materials of Commerce", 1929, Vol. I, p. 380) says that "teak is immune from attacks of white ants and is extremely durable in most climates. When once seasoned it does not warp, split or crack, and is unaffected by contact with iron, owing to the presence of an oil."

From the above it is apparent that considerable confusion exists in forestry literature regarding the oil obtained from teak and the supposed use of 'teak oil' as a substitute for linseed oil would suggest that it is of the nature of a fixed oil. There is practically no reference in chemical literature about the oil obtained either from the wood or from the seeds, except that by Romanis (*J. Chem. Soc.*, 1887, 51, 868) who failed to extract any essential oil from teak wood. There is no doubt that teak wood is attacked by insect borers (white ants, etc.), to much less extent than other common woods and this immunity is probably due to resinous and tarry matters which Romanis (*loc. cit.*) has reported. It is interesting, therefore, to find out if the seed oil has any constituents that might prove of

value as an insecticide. For this purpose the seed oil has been examined but the results obtained do not appear to indicate any constituent, besides the resin acids, to which the insecticidal value could be attributed. The total oil found to be present in the seeds is 0.23% only, of which 5% are resin acids, the quantity of the acids being small their exact identity could not be established.

The teak seeds used in this investigation were obtained from Burma. They had a hard and tough shell containing 4 to 5 kernels a piece of the size and shape of sesame seeds. Ten seers (20 lbs.) of the seed shells on being crushed yielded 50 g. of the kernels which on extraction with ether produced 20.45 g. of a bright red oil. Thus the oil is 41% of the kernels and 0.23% of the seeds. Steam distillation of the seeds yielded no essential oil but only an insignificant amount of a whitish flocculent matter. The red colour of the oil appears to be due to the colouring matter of the shell. The following are the general characteristics of the oil.

Consistency	...	...	...	Liquid
Colour	...	...	...	Bright red
Sp. gr. at 20°	...	...	.	0.9213
Refractive index at 25°	...	...	...	1.4655
Iodine value (Hanus)	...	...	...	107.5
Saponification value	...	...	...	194.5
Hehner value	...	...	...	98.2
Acid value	...	...	...	31.7
Acetyl value	...	...	...	146.1
Unsaponifiable matter	...	...	...	1.25%

*Composition of the fatty acids.*—10 G. of the mixed acids, from which the unsaponifiable matter had been removed, were separated into the solid and liquid acids by the Twitchell's method with the following results:—

(A) Acids whose lead salts were insoluble in boiling 95% alcohol in the presence of acetic acid (mostly resin acids)	...	0.5 g.
(B) Solid acids	...	2.5
(C) Liquid acids	...	7.0

*Chemical constants of the mixed acids.*

Mean M. W.	278		
Iodine value (Hanus)	100	Iodine value.	M. W.
Resin acids	5%	30.5	288
Saturated fatty acids	25%	3.8	275
Unsaturated „ „	70%	146	...

The amount of saturated and unsaturated acids being small, attempts were not made to separate and identify the individual acids by their fractional crystallisations or the fractional distillation of their methyl esters. In the case of liquid acids it was found that on standing the iodine value fell from 146 to 63, making the acids viscous and much less soluble in petroleum ether. The data recorded above appear to indicate that the solid acid portion consists mainly of stearic and palmitic acids and the liquid acid portion consists mainly of oleic and linoleic acids.

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## Colloid Chemical Analysis. Part II.

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MAZUMDAR AND ASUTOSH CHATTERJEE.

In the introduction to the first paper (*J. Indian Chem. Soc.*, 1981, 8, 873) attention has been drawn to the uncertainties regarding the fundamental concepts concerning the electrical properties of colloids. The present paper deals with further experimental work. Theoretical considerations relevant to the subject matter of this paper are briefly referred to as they will be discussed in a series of papers to appear in the *Kolloid Zeitschrift* (cf. Mukherjee, *Kolloid Z.*, 1933, 62, 257; 1933, 63, 36).

### A. Theoretical Considerations.

1. The Helmholtz-Smoluchowski theory of cataphoretic motion gives the specific conductivity,  $K_1$  of a colloidal solution, free from intermicellary electrolytes and neglecting the conductivity of the ions of water, as follows:—

$$K_1 = C \cdot u \quad \dots \quad \dots \quad \dots \quad (1)$$

$C$  is the number of electrochemical equivalents of free charge carried by the colloidal particles per c. c. which is equal to that carried by the mobile ions and  $u$  is the equivalent conductivity of the charged colloidal particle, i.e., the cataphoretic speed multiplied by  $F$ , the Faraday quantity of electricity. According to this theory the mobile ions take no part in the transport of electricity and their transport number is zero while that of the charged colloidal particle is unity. On the other hand according to the chemical school, built up by Duclaux, MacBain and Pauli and coworkers, (*vide* Pauli and Valko, "Electrochemie der Kolloide," 1929, for a systematic exposition) the specific conductivity is given by the following equation

$$K_1 = C(u + v) \quad \dots \quad \dots \quad \dots \quad (2)$$

where  $K_1$ ,  $C$  and  $u$  have the same significance as in equation (1) and

$v$  is the equivalent conductivity of the mobile ions which are assumed to be all of the same kind.

2. The difficulty of ascertaining which of these equations is confirmed by observations rests on the uncertainty of determining the value of  $C$  and to a less extent of  $v$ . In most colloidal solutions intermicellary electrolytes\* are present and the ions associated with the colloid are often partly present as mobile ions in the intermicellary liquid. The specific conductivity  $K$  of such solutions is given by

$$K = K_1 + K_2 \quad \dots \quad \dots \quad \dots \quad (3)$$

$K_1$  and  $K_2$  are respectively the specific conductivities of (a) the charged colloidal particles and their mobile ions and (b) of the intermicellary electrolytes. In order to ascertain the conductivity and composition of the charged colloidal particles and their associated ions, Duclaux, Zsigmondy and MacBain and coworkers assumed that the ultrafiltrate has the same composition as that of the intermicellary liquid. From the differences in the conductivity and composition of the colloidal solution and of the ultrafiltrate, those of the colloid and associated ions are calculated. Pauli pointed out, that the ultrafiltrate should not, from the point of view of Donnan's theory of membrane potential, have the same composition as the intermicellary liquid. He made simultaneous measurements of the activities of ions in the solution. The experimental results which follow show how far-reaching changes can be produced by ultrafiltration (*cf.* Part I, *loc. cit.*). Unfortunately the activity coefficients of ions in these solutions are unknown. A further complication arises from the well known fact, established by the work of Duclaux and MacBain and his coworkers, that part of the ions carrying a charge of opposite sign to that of the colloidal particles moves with the latter in an electric field. The chemical school in analogy with the usual concepts of electrochemistry interprets this fact as indicating incomplete dissociation (classical theory), or, complete ionisation together with a limited association of

\* Duclaux designated the charged colloidal particle together with the associated mobile ions (formed by dissociation in his opinion) as a micelle (*vide* Zsigmondy, *Kolloid chemie*, 3rd Edition, 1920. p. 126). The 'free' electrolytes present in the sol other than the charged colloidal particle and the associated mobile ions were also designated by him as intermicellary electrolytes.

ions (Pauli and Valko, *loc. cit.*). At any rate since the same ions are present in most cases as mobile ions and also as ions of the intermicellary electrolytes, the actual concentration of the mobile ions as such is less and different from their total concentration in the sol.

3. Whereas the chemical school deals with the activities, conductivities, molecular and ionic constitution and related properties, they are rather cursorily discussed in orthodox text books of colloids. The so-called physical school is concerned mostly with potentials of the double layer, its thickness, capacity and changes in interfacial tension. The distribution of the electric charges is considered as in metallic condensers and the actual distribution of the ions is overlooked. The properties of the primarily adsorbed ions including their valencies and the equilibrium distribution of ions between the surface, the mobile layer and the solution, appear to be the main factors whose detailed consideration is necessary for a proper understanding of the electrical properties of colloids. A rational picture of the double layer and the equilibrium distribution of ions on this basis was first discussed by one of us in 1921 (Mukherjee, *Trans. Faraday Soc.*, 1921, 16, 103) and the general outline given there has been developed in subsequent papers. According to this point of view one would expect a characteristic behaviour of colloidal solutions. Briefly stated, the differences with usual simple electrolytes arise out of the distribution of the electrical charges, the adsorption (primary and electrical) of ions and the 'non-homogeneous' (in the sense of Gibbs' phase rule definitions) nature of the interface. For example, mobile ions are thickly distributed adjacent to the colloidal particles and in addition to interionic attraction, formulated by one of us as electrical adsorption (*loc. cit.*), also interionic repulsion has to be considered (*vide* Mukherjee, *Thesis, University of London*, 1921). The electrical potential of the region in which the ion finds itself is a factor determining the activity coefficient of an ion and the manner of distribution of the electrical charges determines this potential. Irreversible and reversible changes arising out of the agglomeration also take place. Besides, the activities of the primary and electrically adsorbed ions, which are either 'actual' or 'possible' components of the surface (in the sense in which these terms have been defined by Gibbs) cannot be interpreted without reference to the interaction with the surface (*Proc. Ind. Science Congress*, 1929, p. 96). This does not necessarily imply that the activity

coefficient is not, in suitable cases, determined by the electrical potential. Another point of difference may be mentioned. It arises out of what is meant by the valency of the charged colloidal particles, the "colloidal" ions of the chemical school (Pauli and Valko, *loc. cit.*, give values for the valency from 10 to 200,000). The total free charge of a colloidal particle is evidently the sum of the charges carried by the primarily adsorbed ions on its surface. Assuming the latter to consist only of ions of one kind, the total free charge would be given by the product of the valency of each ion with the number of such ions on the surface of the particle. According to the chemical school the total free charge denotes the valency of the 'colloidal' ion. It appears that the valency of the primarily adsorbed ions is the more important factor and the valency (*i.e.*, the total charge which from analogy with electrolytic ions gives the valency) of the 'colloidal ion' as a whole has a secondary significance.

*B. The Discrepancy between Activity and Conductivity Measurements in Colloidal Solutions*

1. The measurements of activities and conductivities of ferric oxide sols given in Part I (*loc. cit.*) show that it is difficult to reconcile the observed activities with the conductivities; the latter are too high. The hydrogen ion activity in this sol cannot be directly measured and was determined after coagulation with solid potassium sulphate following Pauli who used potassium chloride. Pauli and Valko (*loc. cit.*, p. 309) also mention that the observed conductivity is high and in some cases requires the assumption of an equivalent conductivity of 118 at 25° for the positive carriers other than hydrogen ions. As no such cation has so far been discovered, this in itself is an observation of considerable interest.

2. The following table gives the conductivities calculated from the measurement at 20.5° given in Part I (*loc. cit.*). The specific conductivities in column 3 (Table I) have been calculated as follows: From the experimentally measured activities of the chlorine ions, their total concentration in the sol in the free state is calculated on the assumption that the activity coefficient is unity. The concentration calculated per c. c. multiplied by the equivalent conductivity of chlorine ions at infinite dilution at 20.5° gives the contribution of these ions to the specific conductivity. The activity of hydrogen ions measured after coagulation gives similarly their contri-

bution to the specific conductivity. Assuming the chlorine ions to be the only negatively charged carriers of electricity, the equivalent conductivity of all the positively charged carriers is given by the excess of the concentration of chlorine ions over that of the hydrogen ions. The positively charged carriers are the charged colloidal particles and possibly usual electrolytic ions containing iron, *e.g.*, ferric ions. As the relative concentrations of these ions are unknown, the contribution of the positively charged carriers has been calculated assuming either that there are no electrolytic ions containing iron or that there are only ferric ions and no other positively charged carriers.

The following equivalent conductivities at infinite dilution at 20.5° have been used:  $H^+ = 327$ ;  $Cl^- = 70.3$ ;  $\frac{1}{3} Fe^{+++} = 64$ . The cataphoretic speed was directly measured by the boundary methods. The large values of the equivalent conductivity cannot be reconciled with the activity measurement.

TABLE I.

Dilution X.	$K_{obs.}$ $\times 10^4$	$K_{calc.} \times 10^4$		$K_{obs.} / K_{calc.}$		$[\Delta_r]_{Cl.}$			
		Colloid ions (1)	Ferric ions (2)			(1)		(2)	
				(1)	(2)	$\gamma$	$\delta$	$\gamma$	$\delta$
1	10.39	4.41	4.69	2.36	2.26	39.5	270.7	21.5	235.7
2	5.60	2.97	3.59	1.88	1.56	54.17	203.4	18.2	166.4
4	3.08	1.37	1.66	2.25	1.86	70.3	243	40.3	213
6	2.17	0.93	1.10	2.33	1.96	76.3	259.3	49.3	232.3
11	1.18	0.59	0.70	2.00	1.7	76.1	206.1	52.1	182.1

The equivalent conductivities  $\gamma$  and  $\delta$  of the chlorine ions have been calculated in two ways: assuming that besides hydrogen ions there are (i) only charged colloidal particles which carry positive electricity and (ii) that alternatively only ferric ions are present. The equivalent conductivity  $[\Delta_r]_{Cl}$  is given as follows:

$$[\Delta_r]_{Cl} = \Delta_r - [\Delta_u]_{coll \text{ or } \frac{1}{3} Fe^{+++}} \quad \dots (4)$$

where  $\Delta_r$  is the equivalent conductivity of the "colloid" chloride and  $[\Delta_u]$  for 'coll,' or,  $\frac{1}{3} Fe^{+++}$ , is that of the "colloidal" ions or of the ferric ions.  $\Delta_r$  has been calculated in two ways:

namely, (a) by subtracting the concentration of the hydrogen ions,  $C_H^\circ$  from  $N_{Cl'}$ , the total chlorine concentration; this gives the total chlorine associated with the colloid ( $\gamma$  value); and (b) by subtracting  $C_H^\circ$  from  $C_{Cl'}$  the concentration of the free chlorine ions (calculated from the activity as stated above).

$$\left. \begin{aligned} \Delta_v &= \frac{1000 \cdot (K - K_{HCl})}{N_{Cl'} - C_H^\circ} & \dots & \gamma \\ \Delta_v &= \frac{1000 \cdot (K - K_{HCl})}{C_{Cl'} - C_H^\circ} & \dots & \delta \end{aligned} \right\} \quad (5)$$

The equivalent concentration of 'colloid' ions or of ferric ions is given by  $C_{Cl'} - C_H^\circ$ .

3. In Part I (*loc. cit.*) a method has been indicated for testing experimentally the hypothesis that the surface density of charge runs parallel, within certain limits, to the cataphoretic speed. This proposition can be reconciled with the Helmholtz-Smoluchowski and the Debye-Hückel theories of cataphoresis (Mukherjee, *Kolloid Z.*, 1933, 62, 263). In view of the uncertainties in determining  $C$  and the activity and conductivity coefficients it is not possible to apply this method till these quantities can be unequivocally ascertained. Other sources of evidence in support of this hypothesis will be discussed elsewhere (*Kolloid Z.*). In order to reconcile the variations of the cataphoretic speed with this hypothesis, the following assumptions were made (the concentration of the colloidal particles is taken to be proportional to the dilution):

(a) The positively charged carriers in the sol consist of hydrogen, ferric (and perhaps other electrolytic ions containing iron) ions and charged colloidal particles. The equivalent concentration of the latter is comparatively small and the observed chlorine ion activity may be attributed to the free chlorine ions, associated with the ferric ions and with the hydrogen ions.

(b) The activity and conductivity coefficients are unity.

(c) The mobility of the charged colloidal particles is to be increased by a constant factor assumed in the calculation to be equal to that of the chlorine ions. The last assumption is quite arbitrary. The above illustrates that the interpretation of the activity and conductivity measurements constitutes the first step towards the theoretical elucidation of the subject.

4. Pauli and Valko (*loc. cit.*, p. 311) refer to the advantage which aluminium oxide sols possess in that the activities of both hydrogen and chlorine ions can be measured. They show (Pauli and Valko, *loc. cit.*, pp. 311-314) that the equivalent conductivity increases regularly with the dilution and that the ratio of the equivalent conductivity to the equivalent activity is constant (*vide* column 4 of Table II which reproduces their data). The constancy of this ratio signifies that throughout the range of dilutions the conductivity coefficient also varies proportionally. Such a coincidence will be remarkable even for a true electrolyte and a difference and not a strict proportionality is expected on theoretical grounds. Besides, the assumption that all the chlorine atoms exist as free ions requires independent experimental proof.

TABLE II.

*Aluminium oxide sol (Pauli and Valko).*

Dilution X.	Equivalent conductivity of 'colloid' chloride.	Equivalent chloridion activity $\times 10^4$ .	Ratio of equivalent conductivity to activity.	Activity coefficient.
1	51.82	28.1	19.5	0.387
2	59.74	30.1	19.8	0.392
4	64.75	318.2	20.5	0.440
8	71.13	348.0	20.4	0.492
16	79.11	370.6	20.3	0.516
32	84.85	394.5	21.5	0.547
64	91.0	431.5	21.6	0.598
128	97.17	469.9	20.6	0.619
256	105.4	483.8	21.8	0.761

5. On calculating their results differences are observed between the measured and calculated conductivities (Table III). It will also be seen that the equivalent conductivity at infinite dilution, calculated on the assumption that the activity coefficient is equal to the conductivity coefficient, regularly decreases at the higher dilutions.

Dilution. X	Sp. conductivity $\times 10^5$		Equiv. conducti- vity at infinite dilu- tion at 25°.
	Obs.	Calc.	
1	400.2	345	141.7
2	218.9	176.1	152.4
4	119	99.4	147.1
8	66.3	56.3	144.5
16	37.4	30.2	153.3
32	20.13	16.6	155.2
64	11.36	9.47	152.2
128	6.4	5.6	143.1
256	3.6	3.26	137.4

The following equivalent conductivities at 25° have been used in the above calculations:  $H^+ = 350$ ,  $Cl^- = 75$ ,  $1/3Al^{+++} = 47$ . The equivalent concentration  $C_{1/3Al^{+++}}$  of aluminium ions has been taken to be equal to  $C_{Al^{+++}}$ .

6. The hydrogen ion concentrations of these aluminium oxide sols are relatively large. Free aluminium ions in solution are probably stable below a  $p_H$  equal to 4 (Britton, "Hydrogen Ion Concentration", 1929) and it is difficult to ascertain the relative proportion of the positive charges carried by aluminium ions and colloidal aluminium oxide.

### C. *The Characteristic Behaviour of Colloids.*

Pauli and Valko (*loc. cit.*) have discussed other observations which show that the conductivities and activities of ions of these colloidal solutions are often difficult to reconcile with each other as also with their osmotic pressures. They, however, conclude (*loc. cit.* p. 817) that the modern theory of interionic attraction together with the assumption of a suitable association factor can explain these differences. The data given in the following pages show that the activities of the ions of these solutions cannot be reconciled with the conductivity. Indeed both the chemical and physical theories fail to account for the observations. These colloidal solutions in fact behave in a manner which characterises them.



The experimental work recorded in this paper deals with the following subjects :

#### EXPERIMENTAL.

(a) The ultrafiltrate of aluminium oxide sols having a relatively high hydrogen ion concentration has been analytically examined. Free aluminium ions are possibly present. The conductivities and the activities of the ions of a number of aluminium oxide sols having increasing  $p_H$  values have been measured and the cataphoretic velocity of the colloid has been also measured by the boundary method. One sol has been titrated with baryta and the change in conductivity,  $p_H$  and chlorine ion activity has been measured simultaneously.

(b) Similar measurements have been made with silicic acid sols.

#### I. Experiments with Sol A. Aluminium Oxide Sols.

*Preparation of the sol.*—The sol was prepared by adding to a litre of normal aluminium chloride solution slightly less than the equivalent amount of normal ammonia solution. A precipitate was formed which on vigorous stirring was stopped and on keeping overnight a perfectly clear sol was formed. The sol was dialysed in a parchment paper against repeated changes of hot distilled water. After dialysis had been continued for about a month and a half the sol was found to be turbid and more suitable for measurements of charge by the boundary method. The dialysis was then stopped.

*Measurements of cataphoretic speed.*—The cataphoretic speed of the colloidal particles was measured by the method of moving boundaries as modified by Mukherjee (*Proc. Roy. Soc.*, 1923, 103A, 102). Aluminium hydroxide sol, however, being colourless, a dark background illumination was devised which enabled the boundary to be distinctly visible. For upper liquid a hydrochloric acid solution was prepared having the same  $p_H$  as the sol. To this acid solution a concentrated solution of aluminium chloride was added drop by drop until the resulting mixture was of slightly greater conductivity than that of the sol. By this procedure the potential gradient and also the upward and downward movements of the boundary was found to remain constant. For the sake of comparison the ultrafiltrate was also employed as the upper

liquid. In this case also the potential gradient remained remarkably constant and the upward and downward movements of the cataphoretic speeds agreed with the results obtained when the other procedure was employed.

*Measurements of chlorine ion concentration.*—The concentration of chlorine ions was determined by means of silver—silver chloride electrodes. The electrodes were prepared according to the method of Noyes and Ellis (*J. Amer. Chem. Soc.*, 1917, **39**, 2532).

*Determination of total chloride.*—The total chloride of aluminium hydroxide sol was determined by potentiometric titration with a standard solution of silver nitrate. A concentration cell was set up with the solution whose total chloride was to be determined and a saturated AgCl solution as the other electrode. Both the solutions contained 5% KNO<sub>3</sub>. The connecting salt bridge was a saturated solution of KNO<sub>3</sub>. The *E.M.F.* gradually decreased and when all the chloride was precipitated by AgNO<sub>3</sub>, the sign of the *E.M.F.* was reversed. The end points were read off from the graphs as usual.

*Hydrogen ion concentration.*—The hydrogen ion concentration of the sol was determined by means of a hydrogen (quinhydrone was also used) electrode. A normal calomel electrode and a K-type Leeds Northrup potentiometer were employed.

*The ultrafiltrates.*—35 C.c. of the aluminium hydroxide sol was filtered through ultrafilters prepared from a high concentration of collodion in an open pattern nickel plated apparatus and 25 c.c. filtrate collected. This is the first portion of the filtrate. The sol left on the ultrafilter was collected separately. Again 35 c.c. sol were placed on the filter and filtered till 25 c. c. of the fresh filtrate were collected. This is the second portion of the filtrate. The sol left on the filter this time was mixed with that of the previous operation and the mixture constitutes the 'residual' sol.

TABLE IV.

*Composition of the sol.*

	Sp. conductivity × 10 <sup>3</sup> .	Activity of Cl ion × 10 <sup>3</sup> .	Total chlorine × 10 <sup>3</sup> .	Hydrogen ion conc. × 10 <sup>3</sup> .
A	1.25	1.1	1.15	0.155
A/2	0.690	0.6	0.567	0.132
A/6	0.221	0.2	0.215	0.0083

TABLE V.

*Composition of the residual sol.*

	Sp. conductivity $\times 10^3$ .	Activity of Cl <sup>-</sup> ion $\times 10^2$ .	Total chlorine $\times 10^2$ .	Hydrogen ion conc. $\times 10^4$ .
A	1.42	1.41	0.32	1.12
A/2	1.03	0.77	0.83	1.02
A/6	0.385	0.28	0.29	0.813

TABLE VI.

*Composition of the ultrafiltrate (first portion).*

A	0.69210	0.741	0.650	0.468
A/2	0.578	0.407	0.363	0.396
A/6	0.189	0.166	0.135	0.347

TABLE VII.

*Composition of the ultrafiltrate (second portion).*

A	0.949	0.813	0.741	0.617
A/2	0.590	0.457	0.285	0.490
A/6	...	...	0.148	...

TABLE VIII.

*Cataphoretic speed of aluminium hydroxide sol with dilution*  
Temp. 35°.

Upper liq.	Dilution.	Upward			Downward		
		Pot. gradient volt/cm	Rate of migration in cms. per sec. per volt/cm. $\times 10^5$ .		Pot. gradient volt/cm.	Rate of migration in cms. per sec. per volt/cm. $\times 10^5$ .	
		Before movement of boundary.	After movement of boundary.		Before movement of boundary.	After movement of boundary.	
Ultrafiltrate	A	0.617	0.626	34.28	0.658	0.692	34.65
	A/6	0.744	0.747	38.1	0.742	0.696	41
HCl + AlCl <sub>3</sub>	A	0.638	0.629	31.9	0.654	0.633	33.9
	A/2	0.724	0.708	44.5	0.691	0.68	44.2
	A/6	0.732	0.712	40	0.69	0.681	43

*Changes on ultrafiltration.*—In agreement with the results obtained with Fe<sub>2</sub>O<sub>3</sub> sols the ultrafiltrate has a different conductivity and composition than the original sol. The conductivity of the residual sol is, however, greater but that of the ultrafiltrate is less. With the ferric oxide sol the residual sol after ultrafiltration had a smaller conductivity (Mukherjee, Roychoudhury and Biswas, *loc. cit.*). The Cl<sup>-</sup> ion concentration of the residual sol is greater with

both sols. Thus with the ferric oxide sol an increase of the  $\text{Cl}'$  ion concentration and the oxide content results in the diminution of the conductivity of the residual sol whereas with the  $\text{Al}_2\text{O}_3$  sol an increase is observed. Evidently the distribution of the ions ( $\text{Cl}'$ ,  $\text{Al}'''$  and  $\text{H}'$ ) between the intermicellary liquid and between the 'liquid' and 'solid' sides of the double layer determines the properties of the sol. The total interface and the  $p_{\text{H}}$  range giving the stability of the cations of the oxide also play an important rôle. It is not possible to specify the properties of such a sol unless we have definite knowledge of these factors which are responsible for the difference between the results of the two sols. Within the observed  $p_{\text{H}}$  range the  $\text{Al}'''$  ions are stable ( $p_{\text{H}}$  3.5, 4.6) and it is not surprising that the total  $\text{Cl}$  and the  $\text{Cl}'$  ion concentration have practically the same value. The sol is rich in electrolytes and the ultrafiltrate contains aluminium and hydrogen chlorides. The constancy of the potential gradient with the ultrafiltrate as the upper liquid (*vide* Table VIII) is to be attributed to the fact that the amount of the current carried by the colloid particles is small compared with that carried by free electrolytes.\*

*Analysis of the aluminium oxide sols.*—The results given above are summarised in the following table;  $u$ , the cataphoretic speed of the colloidal particles;  $U$  the cataphoretic speed multiplied by one Faraday;  $K_{\text{obs.}}$ , the observed specific conductivity;  $C_{\text{Cl}'}$ , the activity of  $\text{Cl}'$  ion;  $N_{\text{Cl}}$  the total chloride concentration;  $C_{\text{H}^+}$ , the concentration of  $\text{H}'$  ion;  $C_{\frac{1}{3}\text{Al}'''}$  the concentration of  $\frac{1}{3}\text{Al}'''$  (assuming that  $C_{\frac{1}{3}\text{Al}'''} = C_{\text{Cl}'} - C_{\text{H}^+}$ ).

TABLE IX.

Dilution.	$u \times 10^{-6}$ .	$U$ .	$K_{\text{obs.}}$	$C_{\text{Cl}'}$ .	$N_{\text{Cl}}$ .	$C_{\text{H}^+}$ .	$C_{\frac{1}{3}\text{Al}'''}$ .
A	37.3	36.5	0.00125	0.011	0.0106	0.000155	0.010845
A/2	48.0	46.34	0.00069	0.00617	0.00567	0.000132	0.006038
A/6	41.3	39.57	0.000221	0.00234	0.00215	0.000093	0.002247

## II. Experiments with Sols D, L and M.

*Preparation.*—A precipitate of aluminium hydroxide was obtained by adding one litre of 0.1N-ammonia solution to 1 litre of

\* Mukherjee, Roychoudhury and Biswas (*loc. cit.*) have shown that the ultrafiltrate of the sol is not always satisfactory as an upper liquid for cataphoretic measurements by the moving boundary method.

0.1N-aluminium chloride. The precipitate was washed with conductivity water 9 times with the help of a powerful centrifuge. The containers were of borosilicate glass. The supernatant liquid was thrown off and the precipitate resuspended in conductivity water. In the last two washings the precipitate was suspended in 600 c.c. of water. The supernatant liquid containing colloidal aluminium oxide after the last operation of the centrifuge, was allowed to stand for 15 days and the stable sol consisting of the supernatant liquid was siphoned off (sol D). The precipitate in the container was mixed with 50 c.c. of water and 30 c.c. of the suspension were divided into portions of 10 c.c. each. All three were diluted with 500 c.c. of conductivity water. To one of these three no hydrochloric acid was added: the sol thus obtained gives sol  $K_0$ . To the other two, 5 c.c. and 1 c.c. respectively of 0.005N-HCl were added and the sols thus obtained give sols  $L_0$  and  $M_0$  respectively. The object of the repeated washings was to remove traces of ammonia as far as possible. 400 C.c. of sol  $L_0$  was diluted to 1600 c.c. with conductivity water and stocked in an atmosphere of hydrogen free from carbon dioxide, or air. This sol is sol L. Sol M was similarly obtained from sol  $M_0$ .

*The accuracy of the chlorine ion activities.*—It has been seen in Part I that calomel and silver chloride electrodes give reliable and mutually agreeing values of the chlorine ion activity. The measurements of the chlorine ion activity in dilute hydrochloric acid solutions by the calomel electrode is rendered uncertain on account of the reaction of the dissolved oxygen (Mukherjee and Kumar, *J. Amer Chem Soc.*, 1930, 52, 2179). The agreement between the calomel and silver electrodes mentioned above shows that in colloidal solutions of ferric oxide this disturbing effect is negligible. It was, however, thought desirable to prepare silver chloride electrodes in the several ways used by previous workers for the most accurate measurements and to compare the results so obtained with those with calomel electrodes. The chlorine ion activities of hydrochloric acid at two dilutions were measured with these electrodes and care was taken to render the system free from oxygen. The *E.M.F.* of the "concentration" cell is reproducible within 0.1 millivolt. The following data show the agreement between tested silver chloride electrodes and the calomel electrode.

cell :  $\text{Ag/AgCl/0.000353N-HCl/sat. KNO}_3/0.00353\text{N-HCl/AgCl/Ag}$   
 Observed *E.M.F.* = 0.0610 volt at 35°.  
 With  $\text{Hg/HgCl}$  electrodes *E.M.F.* observed = 0.0595 volt.

The *E.M.F.* calculated from the activity coefficients given by Randall and Young for 25° (*J. Amer. Chem. Soc.*, 1928, 50, 989) is 0.05943 volt.

The concentrations of the free chlorine ions of sols L and M calculated from the observed activities are very low (of the order of  $10^{-5}$ ). It is well known that the measurement of chlorine ion activities by the silver—silver chloride or calomel electrodes at such low chlorine ion concentrations of simple electrolytes (e.g., hydrochloric acid or potassium chloride) is uncertain. Both the silver—silver chloride and the calomel electrodes, however, gave activities which agree sufficiently well with each other. The *E.M.F.s* actually observed against 0.009353N-HCl are given below.

The cell combination was as follows :

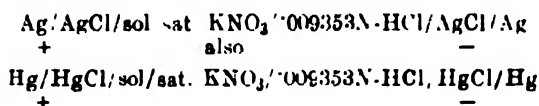


TABLE X.

*Aluminium hydride sol, sample L.*

Dilution.	Ag—AgCl	Electrode.	Hg—HgCl	Electrode.
	Time.	<i>E.M.F.</i> in volts.	Time.	<i>E.M.F.</i> in volts.
L	2.15 p.m.	0.1220	1.45 p.m.	0.1420
	3	0.12075	2	0.1420
	3.15	0.1425		
	3.30	0.1425		
L/2	4	0.0750	2.15	0.1285
	4.15	0.1210	2.45	0.1370
	4.30	0.1380	3.15	0.1370
	4.45	0.1380		
L/4	5	0.1075		0.1195 (constant value)
	5.15	0.1195		
	5.30	0.1195		
L/6	4.15	0.0825		0.1090
	5	0.0705		0.0720
	5.15	0.0705		0.1095
				0.1140 (constant value)

\* The time readings were not taken.

TABLE XI.

*Aluminium hydroxide sol, sample M.*

Dilution ...	M	M/2	M/6	M/11
Ag—AgCl electrode } ...0.1809 (const. value)	0.2073	0.2080	0.2760	
E.M.F. in volts. }				
Hg—HgCl electrode } .. 0.1802 (const. value)	0.2010	0.2045	0.1877*	
E.M.F. in volts. }				

The concentration of the total chloride was determined as before by electrometric titration which gives the best reproducibility. In some cases the chlorine ion activity of the sol treated with nitric acid and diluted to a known volume was also measured and the concentration was calculated. Care was taken to avoid loss of chlorine in dissolving the colloid in nitric acid. Volhard's method was also used. Electrometric titrations give the best results.

The arrangements for stocking the sol in an atmosphere of carefully purified hydrogen as also the difficulties arising out of the presence in the sol and leakage of carbon dioxide in titrations with alkali have been described elsewhere (Mukherjee, Roychoudhury, Das-Gupta, and Chatterjee, *Ind. Journ. Agric. Sci.*, 1932, 2, 638). The arrangements for simultaneous measurements of chlorine and hydrogen ion activities as also of the conductivity in an atmosphere free from oxygen or carbon dioxide in such titrations, of sol D have been described in the above paper. Only the results are given in this paper.

In the following tables the symbols have the significance given below:

$C_{Cl}$  = the concentration of chlorine ions in g. ions per litre calculated from the observed activity assuming the activity coefficient to be unity.

$N_{Cl}$  = the total chlorine concentration in g atoms per litre.

$K_{obs}$  = the measured specific conductivity;  $u$  = the equivalent conductivity of the charged colloidal particles obtained from the measured cataphoretic speed.

$C_H$  = the concentration of hydrogen ions calculated as in the case of the chlorine ions.

$C_{coll}$  or  $C_{\frac{1}{2}Al^{+++}}$  = the equivalent concentration of the charged colloidal particle or the aluminium ion calculated as in the case of the ferric oxide sols (Part I); the symbol  $K$  stands for specific conductivities. The dilution is given as the ratio of the volume of the resulting sol to the volume of the initial sol.

\* A very unsteady reading was obtained.

TABLE XII.

Sol.	Dilution.	$K_{\text{obs}} \times 10^5$ .	$\text{C}_{\text{Cl}'} \times 10^5$ .	$N_{\text{Cl}} \times 10^5$ .	$C_{\text{H}^+} \times 10^5$ .	$u$ .
<div style="display: flex; justify-content: space-around; border-top: 1px solid black; border-bottom: 1px solid black;"> <span>Hg/HgCl</span> <span>Ag/AgCl</span> </div>						
D	Nil	4.94	—	2.17	2.45	0.457
L	"	0.131	4.01	3.95	40.4	0.0097
"	2	0.0887	4.85	4.62	20.2	0.0155
"	4	0.0764	9.57	9.39	10.1	0.0182
"	6	0.0606	11.56	Unreliable	6.7	0.018
M	Nil	0.0546	0.9541	0.928	9.13	0.107
"	2	0.0506	0.3886	0.343	4.57	0.0158
"	6	0.0415	0.3816	0.334	1.52	0.01
"	11	0.0406	Uncertain	0.93	0.00048	

The agreement in the determination of the total chlorine in suitable cases by the different methods mentioned above is illustrated by the following data for sol I.

Volhard's method:  $3.95 \times 10^{-4}$ ; electrometric titration  $4.04 \times 10^{-4}$ .

The aluminium contents of these sols in g. moles of aluminium oxide per litre are as follows:

sol = 0.000122; sol L = 0.000334; sol M = 0.00037.

### III. Experiments with Silicic Acid Sols.

The electrochemical properties of colloidal solutions of acidic and basic substances and of suspensions of such substances are being investigated in this laboratory with reference to a theoretical elucidation of the titration curves and allied reaction of colloidal acid clay. Details of these experiments are given elsewhere (Mukherjee and coworkers, *Ind. Journ. Agric. Sci.*, 1932, 2, 639 and results to be published later). For the purposes of the present paper measurements similar to those described above and carried out with a silicic acid sol (S) \* and its dilutions are given below.

TABLE XIII.

Dilution.	$K_{\text{obs}} \times 10^4$ .	$C_{\text{Cl}} \times 10^4$ .	$N_{\text{Cl}} \times 10^4$ .	$C_{\text{H}^+} \times 10^4$ .	$N_{\text{Na}^+} \times 10^4$ .	$u \times 10^5$ .
S.	11.2	41.8	52	83.2	54	...
S/2	5.98	21.4	...	10.7	...	16.5
S/6	2.57	7.8	...	2.2	...	10.8

\* The method of preparation of the sol is as given by Mukherjee, Roychoudhury Das-Gupta and Chatterjee (*loc. cit.*).



*Calculations.*

In the following calculations the equivalent conductivities at infinite dilution and at 35° have been assumed to be as follows:

For sol A, its ultra filtrate and residual sol, sol D and the silicic acid sols,  $H^+ = 404$ ;  $Cl^- = 93$ ;  $1/3 Al^{+++} = 55$ ;  $Na^+ = 64$ ; for sols L and M and their dilutions the values have been used as follows:  $H^+ = 397.5$ ;  $Cl^- = 89.6$ ;  $1/3 Al^{+++} = 53.6$ . The broad conclusions arrived at are not affected by uncertainties in these values and by the limits of experimental error.

TABLE XIV.  
*Aluminium oxide sols.*

Sol.	$K_{obs} \times 10^4$ .	$K_{calc.} \times 10^4$ .			$\Delta_v$	
		Al <sup>+++</sup>		Coll.	$\gamma$ $\delta$	
		(1) Hg/HgCl.	(2) Ag/AgCl.			
A	12.5	...	16.8	14.8	103	108.2
A/2	6.9	...	9.34	8.83	113	104.5
A/6	2.21	...	3.29	2.94	85	92.1
A ultra 1	8.93	...	11.13	...	...	117
A/2 ultra 1	5.78	...	6.16	..	...	137
A/6 ultra 1	1.89	...	2.57	...	...	103
A ultra 2	9.5	..	12.25	...	...	114
A/2 ultra 2	5.9	...	6.84	...	...	125
A 'residual'	14.2	..	21.3	...	...	90.3
A/2 'residual'	10.3	...	11.8	...	...	122.8
A/6 'residual'	3.85	...	4.43	...	...	126.5
D	0.494	...	0.048	0.043	134	156
L	0.0131	0.0574	0.0569	...	3.1	32.5
L/2	0.00887	0.0393	0.667	...	4.0	17.6
L/4	0.00744	0.137	0.134	...	6.8	7.2
L/6	0.00606	0.1661	0.0652	...	7.7	4.5
M	0.00546	0.01719	0.01696	...	0.27	3.02
M/2	0.00506	0.00596	0.00545	...	9.4	131
M/6	0.00415	0.00555	0.00512	...°	24.2	113
M/11	0.00406	...	...	...	47.8	—

TABLE XV.  
*Silicic acid sol.*

Dilution.	$K_{obs.} \times 10^4$ .	$K_{calc.} \times 10^4$ .	$K_{obs.}/K_{calc.}$
S	11.2	43.9	0.261
S/2	5.93	6.32	0.71
S/6	2.57	2.32	1.1

The silicic acid sol was prepared by dialysis from sodium silicate and hydrochloric acid and contained sodium chloride.

#### DISCUSSION.

The calculations given above show that there is a discrepancy between the observed and calculated conductivities. The observations with the ultrafiltrate and the residual sols also show a discrepancy. Greater care was taken in the measurements with sols D, L and M, and those with A formed the first measurements. It will be seen (a) that the observed conductivity is sometimes too high to be accounted for by the activities, *e.g.*, the ferric oxide sols; (b) that it is too small, *e.g.*, aluminium oxide sols, (c) and also the intermediate case where a good agreement is observed. The discrepancy cannot be accounted for by the possible errors in these measurements and in the calculation, as in some cases the difference is too large. The calculated values of the equivalent conductivity per free chlorine ion are widely different.

The sols having a higher  $p_H$  value, *e.g.*, M and its dilutions are likely to contain very few free aluminium ions in the intermicellary liquid and it is with these sols that one observes a very low equivalent conductivity calculated in the manner used by Pauli and Valko (*loc. cit.*).

In these calculations a correction is necessary for the conductivity of the water. The conductivity of the hydrogen ions has been taken into account, only that due to the hydroxyl ions has to be included. Its magnitude is small (excepting  $M_{11}$ ) and its omission does not interfere with the broad conclusions. The dissociation of aluminium oxide as an ampholyte may also be overlooked for our present purpose; because the sum of the conductivities of the ions whose activities have been measured, *e.g.*, in the case of M, is already *several times* greater than the observed value. The increase in the hydrogen and chlorine activities observed with the dilution of sol L is remarkable. So far as the hydrogen ion activity is concerned this is not new. Such an increase has been observed with thorium oxide sol (Pauli and Valko, *loc. cit.*, p. 316) but the increase of the activity of the chlorine is remarkable.

The rapid decrease with dilution in the activity of the hydrogen ions (which are the mobile ions in the double layer) in the case of the silicic acid sol, is in contrast to the above mentioned

behaviour of the chlorine ions. This rapid increase of the hydrogen ion activity with the concentration has no parallel with known acids, strong, medium or weak. It is remarkable that the discrepancy between the observed and calculated conductivities increases rapidly with the concentration of the colloid. The cataphoretic speed of the original sol could not be determined as the sol was lost. An equivalent conductivity of 20 has been assumed in the calculation.

The following results have been obtained by Mr. B. R. Majumdar with a different sample of silicic acid sol. Both hydrogen and quinhydrone electrodes were employed for measurement of the  $p_H$  values.

TABLE XVI.

*Silicic acid sol (T).*

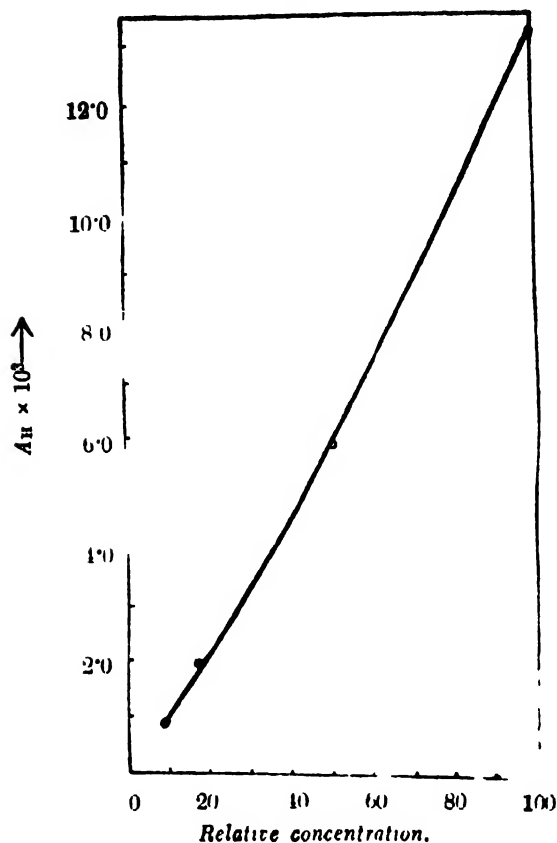
Conc. = 0.1276 g. mol per litre.

Dilution	$A_H \times 10^3$ , (Fig. 1)	$p_H$ .*
T	13.21	1.879 ( $H_2$ electrode) 1.96 (Quinhydrone electrode)
T/2	5.889	2.23 ( $H_2$ electrode) 2.33 (Quinhydrone electrode)
T/6	1.897	2.72 ( $H_2$ electrode) 2.41 (Quinhydrone electrode)
T/11	0.839	3.076 ( $H_2$ electrode) 3.077 (Quinhydrone electrode)

The variation of the  $H^+$  ion concentrations of the sol (Fig. 1) with its concentration confirms the previous observation (*Ind. Journ. Agric. Sci.*, 1932, 2, 638) that the sol behaves as an 'ultra-strong' acid. The increase in the activity of the hydrogen ions at a rate greater than the concentration has no parallel with any known acid in true solution. Moreover, the sol contains free electrolytes, hydrochloric acid and sodium chloride. The concentration of these

\* This column shows the agreement between the values of  $p_H$  obtained by the hydrogen and quinhydrone electrodes.  $A_H$  values in the table are, however, calculated from the  $p_H$  values obtained by the hydrogen electrode.

FIG. 1.



electrolytes increases proportionately with that of the sol. Consequently in these dilute solutions on account of the increasing ionic strength, the activity coefficients should decrease more rapidly than they would with the concentration of dilute solutions of hydrochloric acid. It may be suggested that the stronger acidity is apparent and arises from an actually lower concentration of dissolved hydrogen at the immediate neighbourhood of the Pt-surface. The adhesion of a coating of flocculated particles of the sol on the surface diminishes the rate of diffusion of the hydrogen to the surface and the dissolved hydrogen at the surface is thus not in equilibrium with the gas. Against this is the fact that the sol is quite liquid, and there is no visible sign of flocculi on the electrode surface. What is more decisive is that the  $p_H$  values of the sol by both the quinhydrone and hydrogen electrodes agree. Rabinowitsch and Laskin (*Z. physikal. Chem.*, 1928, 134, 387) have also found that both electrodes give results in mutual agreement. These facts go against

another possible explanation, namely, that there is a greater concentration of the primary particles of the sol on the electrode surface resulting from gelation but no diminished  $H_2$  pressure. In case, gelation or diminished hydrogen pressure was responsible for the observed curvature, both quinhydrone and hydrogen electrodes could not have given identical  $p_H$  values. The results therefore leave no doubt as to the real nature of the manner of increase in the activity with the concentration and of the manner of the variation of the activity coefficient. Further investigations are necessary to find out how far this is due to a progressive replacement of the primarily adsorbed hydrogen ions by the increasing concentrations of sodium ions (*J. Indian Chem. Soc.*, 1925, 2, 191; *Kolloid Z.*, 1929, 49, 362)

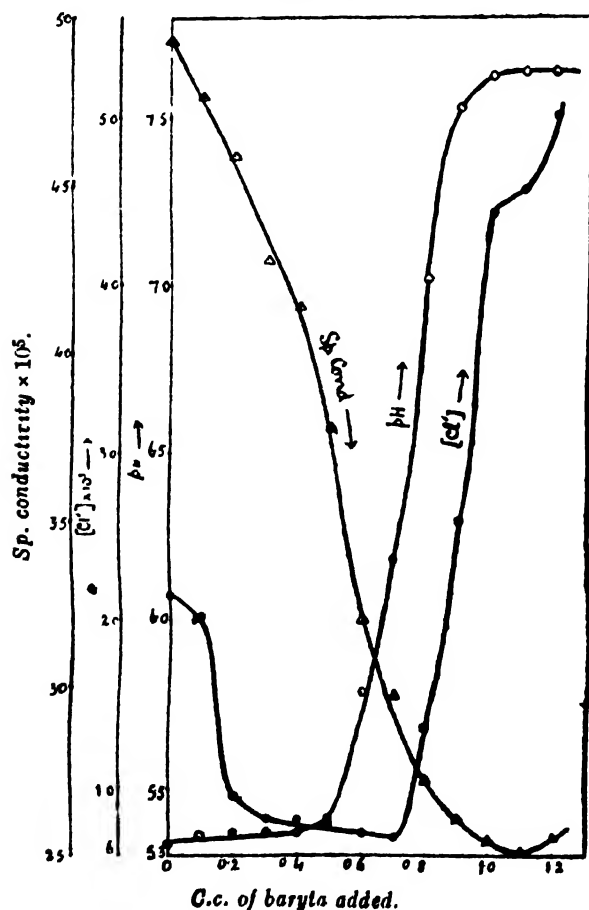
The 'chemical' theory does not contemplate discrepancies of the type revealed in the above calculations. The analogy with electrolytic systems fails in the case of the sols with higher  $p_H$ . Neither can the Helmholtz-Smoluchowski theory account for the higher value of the observed conductivity, *e.g.*, in the case of ferric oxide sols, nor can it account quantitatively for the very low values of the equivalent conductivity. It is possible to imagine that the activity measurements indicate concentrations different from those used in the calculations. The agreement between the total chlorine concentration and that calculated from the activity renders this explanation doubtful in cases where such an agreement has been observed. The other possibility is that the calculation of the hydrogen ion concentration from activity is at fault. But this cannot explain the extremely low equivalent conductivity observed with sol M. Here the equivalent conductivity obtained by dividing the observed sp. conductivity (multiplied by 1000) by the chlorine ion concentration is about 59. The equivalent conductivity calculated similarly for  $M_2$  and  $M_6$  are respectively 147 and 124. This difference cannot be referred to a special error in the measurements with sol M. Sols  $L_1$ ,  $L_2$ ,  $L_4$ , and  $L_6$  have the values 32.6, 18.3, 7.98 and 5.2. These extremely low values are irreconcilable with the Helmholtz-Smoluchowski theory provided the calculated chlorine ion concentration really indicates the actual value.

The cataphoretic speeds change in an irregular manner with the dilution. This is in contrast with the uniform decrease in the specific conductivity observed on dilution in all cases. It is not possible to account for the variations in the cataphoretic speed as arising out of changes in the ionic strength as Pauli and Valko

(*loc. cit.*) have assumed to be the case. The simultaneous measurement of the cataphoretic speed renders invalid the main assumption of Pauli and Valko (*loc. cit.*) that the equivalent conductivity of the colloid ion can account for the observed conductivity. The colloidal ion behaves in a specific manner with respect to its conductivity; also the associated free ions (the mobile ions) show a characteristic behaviour with reference to their activities and conductivities.

The Figure 2 shows the changes in the chlorine and hydrogen ion activities and of the conductivity (all measured simultaneously in an atmosphere of very pure hydrogen) of sol D on titration with a baryta solution. It will be seen that (a) the free positive charges reacting with the hydroxyl ions is less than that calculated from the total chlorine or the chlorine ion activity, and (b) there is a diminution in the chlorine ion activity on the

FIG. 2.



addition of the first amounts of the baryta. These observations go against the assumption of an activity coefficient of about unity for the chlorine ions, which is apparently indicated by the agreement between the total chlorine and the chlorine ion concentration calculated from the activity measurements.

It is necessary to state here that the concentrations of hydrogen and chlorine ions have been calculated from their activities which are fairly reproducible and the observed *E.M.F.s.* were satisfactorily steady. The liquid junction potential though small is unknown and there is a magnification of the error in calculating the concentration of the ions from their activities which are logarithmic functions of the concentrations. It thus becomes necessary only to emphasise those cases where the difference between the calculated and observed conductivities cannot be accounted for by these uncertainties. The magnification of error in calculating the concentration of the ions from their activities obviously depends on the value of the mantissa of the logarithm. It ranges in most cases from 6 to 18% assuming an error of 2 millivolts in the *E. M. F.* The data given above show that the discrepancy is, at least in some cases, too great to be accounted for by these uncertainties. Sol D (*vide* Table XIV) forms a very exceptional example. The specific conductivity of  $9.5 \times 10^5$  is more than ten times greater than the calculated one. One finds similar extremes also in Muttone and Pauli's data (*Kolloid Z.*, 1931, **57**, 212). The figures given in the following table (XVII) have been calculated from the values given by Muttone and Pauli (*loc. cit.*) in Table V of their paper. It will be seen that for sol 5, the observed specific conductivity is ten times the calculated one.

The behaviour of these colloidal solutions presents features not met with usual electrolytes and further investigation is necessary to elucidate the characteristics of some systems.

TABLE XVII.

Sol.	Conc. of $Al_2O_3$ in g. mole per litre.	$A_H$ .	$A_{Cl}$ .	$A_{1/3Al} \dots$ or $A_{colloid} = A_{Cl} - A_H$ .	$A_H \times 394 = X$ .	$A_{Cl} \times 75.4 = Y$ .	$A_{1/3Al} \dots \times 150 = Z$ .	$n \times 10^5$ cm. sec. per volt/cm.	$U = (n \times 96540)$ .	$Z = A_{colloid} \times U$ .	Observed sp. conductivity $\times 10^3$ .	Calc. sp. conductivity $\times 10^3$ . $X + Y + Z$ .	$X + Y + Z$ .
1	0.2451	$3.01 \times 10^{-5}$	$5.8 \times 10^{-1}$	$5.798 \times 10^{-2}$	$7.015 \times 10^{-3}$	4.373	2.044	39.02	37.67	2.154	11.5	7.024	6.5642
2	0.2254	$1.40 \times 10^{-5}$	$4.5 \times 10^{-2}$	$4.499 \times 10^{-2}$	$4.484 \times 10^{-3}$	3.393	2.051	25.55	24.09	1.111	9.5	5.449	4.5089
3	0.2480	$6.81 \times 10^{-6}$	$3.25 \times 10^{-2}$	$3.249 \times 10^{-2}$	$3.376 \times 10^{-3}$	2.451	1.141	21.87	21.1	0.6855	9.1	3.934	3.1389
4	0.2941	$4.90 \times 10^{-6}$	$2.5 \times 10^{-2}$	$2.499 \times 10^{-2}$	$1.71 \times 10^{-3}$	1.885	1.14	14.85	14.34	0.3583	8.2	3.0267	2.2450
5	0.3594	$4.70 \times 10^{-6}$	$6.67 \times 10^{-3}$	$6.665 \times 10^{-3}$	$1.64 \times 10^{-3}$	0.5029	0.304	16.04	15.84	0.1031	6.05	0.8085	0.6076



## SUMMARY.

1. In continuation of the first paper of this series it has been shown, that contrary to the assumptions of the supporters of the chemical school, the conductivity and activity measurements of colloidal solutions of ferric and aluminium oxide sols show characteristic differences from the known behaviour of electrolytes. The measured specific conductivity is in some cases (a) too great, and (b) in other cases too small to be reconciled with the activity measurements. The intermediate case of a satisfactory agreement is also observed.

2. The experimental evidence in support of the above statement is as follows:

(a) The specific conductivities of the ferric oxide sols, the activities of the ions which have been given in Part I, have been calculated from the latter. The values so obtained are very much lower than the observed specific conductivities. This statement is in agreement with the observations of Pauli and coworkers that the observed specific conductivity of some ferric oxide sols required an equivalent conductivity of 118 units at 25° for the positively charged carriers of electricity present in the sol. No such cation is so far known in electrochemistry. Unfortunately the hydrogen ion activity of these solutions cannot be directly measured and Pauli and coworkers measured it after coagulations with potassium chloride. In the experiments in Part I the coagulation was carried out with potassium sulphate. It has been observed from this laboratory that the  $p_H$  of the supernatant liquid depends on the coagulating electrolyte and to a lesser extent on its amount. The  $p_H$  increases comparatively slightly on the addition of larger amounts of the solid electrolyte. It is thus likely that the sol has a different and perhaps a higher hydrogen ion concentration than that estimated by the above mentioned indirect method. It is, however, doubtful whether the actual  $p_H$  of the sol is so low as to account for the observed conductivity.

(b) Aluminium oxide sols have the advantage that the hydrogen ion activity can be directly measured. Pauli and Valko (*loc. cit.*) have shown that this sol shows a constant proportionality between the equivalent activity and the equivalent conductivity of the colloid chloride. They arrive at an equivalent conductivity of about 145

units for the colloid chloride at  $25^{\circ}$  which signifies that the cataphoretic speed of the colloidal particles should be about 70 units at  $25^{\circ}$ . On calculation from their data one finds that the observed conductivity is systematically *lower* than that calculated from the activities assuming that the activity coefficient is equal to unity. It is also found that the equivalent conductivity at infinite dilution calculated according to the assumptions made by them decreases with the higher dilutions. This sol used by them had  $p_{\pi}$  values ranging from 2 to 4. As free aluminium ions are likely to be present in considerable quantities in such solutions, evidence for their presence has been sought to be obtained from the analysis of the ultrafiltrate. Experiments have been described with sols having higher  $p_{\pi}$  and these show that there is a real discrepancy between the activity and the conductivity measurements. The equivalent conductivity of the colloid chloride is sometimes very low, in fact so low that the Helmholtz-Smoluchowski theory which contemplates that the current carried by the charged colloidal particle and its associated mobile ions is wholly measured by the cataphoretic speed multiplied by the free charge of the particle, cannot also account for these low values. The significance of the activity measurement has been briefly discussed.

(c) Observations with silicic acid sols (S) corroborate the above conclusions.

(d) Results of further experiments with a silicic acid sol (T) containing sodium chloride confirm that the activity of the hydrogen ion increases more rapidly than the concentration of the sol, although the total concentrations of electrolytes in the sol correspond to the region of dilute solutions.

(e) Calculations of the specific conductivities of aluminium hydroxide sols from the data obtained by Muttone and Pauli *loc. cit.*) also show considerable discrepancy between the observed and calculated specific conductivities.

(f) Colloidal solutions thus show a behaviour characteristic of themselves and further investigations are desirable.

# Variation of the Charge of Copper Ferrocyanide Hydrosol in Presence of Electrolytes and Non-electrolytes

By S. G. CHAUDHURY.

The investigations on the cataphoretic velocity and coagulation of different hydrosols (Mukherjee and Chaudhury, *J. Indian chem. Soc.*, 1925, 2, 296 ; Mukherjee, Chaudhury and Raichoudhury, *ibid.*, 1927, 4, 493 ; Mukherjee, Raichoudhury and their coworkers, *ibid.*, 1928, 5, 697, 735) produced results not in harmony with current theories on coagulation of colloids in several aspects and it was felt desirable to carry out similar experiments in the case of copper ferrocyanide hydrosol (*cf.* Duclaux, *J. chim. Phys.*, 1907, 5, 29 ; 1909, 7, 405 ; Pappada, *Kolloid Z.*, 1911, 9, 137 ; Sen, *J. Phys. Chem.*, 1925, 29, 517, 539 ; Mehrotra, *Z. anorg. Chem.*, 1925, 142, 345 ; Weiser, *J. Phys. Chem.*, 1926, 30, 1527)

## *Dependence of the Cataphoretic Velocity on the Method of Preparation of the Sol.*

It has been established in the case of arsenic sulphide and ferric hydroxide hydrosols that the cataphoretic velocity depends on the method of preparation of the sol (Mukherjee and Chaudhury, *loc. cit.*; S. N. Mukherjee, *Kolloid Z.*, 1930, 53, 159 ; 1930, 52, 18), and hence different samples of hydrosols of copper ferrocyanide were prepared and their cataphoretic velocities studied. First, the hydrosol of copper ferrocyanide was prepared by precipitating copper ferrocyanide from copper sulphate and potassium ferrocyanide. The precipitate was repeatedly washed with conductivity water till peptisation occurred. The peptisation occurred at a pH value of about 7.5 of the supernatant liquid. The sol obtained in this way is very dilute and in order to obtain a moderately concentrated sol, a few c.c. of a dilute solution of potassium ferrocyanide were added to peptise a given amount of the precipitate. The sol,

so obtained, was subjected to dialysis, till the dialysate gave no test or ferrocyanide. With the progress of dialysis, measurements of cataphoretic velocities were taken. An equiconducting solution of potassium chloride was found suitable as the upper liquid, as the potential gradient before and after passage of the current remained constant within 5%, the direct and reverse readings being also correct within the same percentage of error as shown by the following data in Table I. *In this as well as in subsequent tables  $V$  always denotes the velocity in cm. per sec. per volt per cm. multiplied by  $10^5$ .*

TABLE I.

Samples.	Direct		<i>V</i>	Reverse		<i>V</i>
	Pot. gradient in volts per cm.			Pot. gradient in volts per cm.		
	Before	After		Before	After	
1	0.338	0.813	41.8	0.799	0.845	39.2
2	1.157	1.154	44.9	1.105	1.184	40.8

It will be seen from the Table I that though the potential gradient is not absolutely constant, the variation is not such as to affect the general trend and is within what one obtains in usual measurements of cataphoretic speed unless special care is taken in selecting the upper liquid. One notices that there is always a greater variation with the current reversed. The values for the cataphoretic velocity of the sol with dialysis are given below.

TABLE II

Days of dialysis.	$V$			Equicoagulating conc. of KCl.
	Direct.	Reverse.	Mean.	
0	39.2	41.8	40.5	1.01N
7	44.9	40.8	42.8	1.015
20	45.9	48.8	44.9	0.98
30	50.4	48.4	49.4	0.93
60	48.7	48.3	48.5	0.95

The results show that on dialysis, the cataphoretic speed increases at first and then decreases with progressive dialysis. The coagulating concentration of potassium chloride remains constant for about a week and then diminishes. This observation is not in harmony with the idea that the cataphoretic velocity and the stability of a sol always go hand in hand. Sols designated afterwards as type A were prepared in the above way.

Since by the above procedure, it was found that the sol even after continued dialysis contained appreciable amounts of potassium ferrocyanide, we adopted a different procedure. The precipitate of copper ferrocyanide, obtained from equivalent quantities in solution of copper chloride and potassium ferrocyanide (Weiser, *loc. cit.*), was mixed thoroughly with pure conductivity water and centrifuged. The supernatant liquid was replaced by fresh conductivity water and the process repeated about seven times. After the fourth washing, the precipitate begins to peptise. After two to three further washings, conductivity water was poured very slowly over the precipitate in the centrifuge tube and the clear water, drawn by a pipette, when tested for chloride or ferrocyanide ions was found to be free from them. These precipitates were then mixed with a suitable quantity of water so as to peptise the whole quantity of precipitate and a somewhat dilute sol was obtained. The electrical resistance of the freshly prepared sol was found to be about 10,000 ohms. The resistance decreased rapidly and within one day attained a value of about 6000 ohms. Measurement of the cataphoretic velocity was undertaken with equiconducting potassium chloride as the upper liquid. But here as will be found from the Table III given below, the potential before and after passage of the current was not constant. In this case a few drops of dilute potassium hydroxide solution was added to a solution of potassium chloride such that the conductivity and  $p_H$  of this mixture are equal to those of the hydrosol coagulated with solid KCl. The  $p_H$  of the hydrosol was measured by the colorimetric method after coagulating the sol with the least amount of solid potassium chloride. It is also of interest to note that with (KOH + KCl) mixture as the upper liquid, the potential gradient was found to be fairly constant when the current was first passed for about 15 to 20 minutes before taking the actual readings, and the direct and reverse readings were found to be correct within an accuracy of about 5%.

TABLE III.

Upper liquid.	Direct.		V.	Reverse.		V.
	Pot. gradient			Pot. gradient		
	Before.	After.		Before.	After.	
(1) Equiconducting KCl	0.964	0.912	38.2	0.898	0.952	54.4
(2) Equiconducting mixture of KCl & KOH	0.869	0.836	44.3	0.886	0.912	40.0
	0.850*	0.774	43.7	0.898	0.917	43.4

Sols prepared in the above way are designated henceforward as type B. It was soon observed that this sol on keeping showed clear sedimentation at the bottom. The sol was therefore centrifuged and the cataphoretic velocities of centrifuged and non-centrifuged sols were measured and compared. It was found that (Table IV) centrifuged sols have a little less cataphoretic velocity and they were always found to be more conducting.

TABLE IV.

Nos.	Before centrifuge			After centrifuge		
	Direct.	Reverse.	Mean.	Direct.	Reverse.	Mean.
1	53.6	48.8	51.2	48.4	48.0	48.2
2	46.5	48.9	45.2	42.5	38.8	40.4
3	51.8	48.6	50.2	48.6	45.4	47.0

The data given in the above tables show the dependence of the cataphoretic velocity of the particles of the different sols on the method of preparation.

*Effect of Some Simple Electrolytes and of Centrifuge on the Cataphoretic Velocity of the Sol.*

Effect of some simple electrolytes and centrifuge in their presence on the cataphoretic velocity of copper ferrocyanide hydrosol (in one case type B and in another type A) has been studied. Results are given in the following tables, where *C* denotes the concentration

\* Potential measurement was taken just after the passage of the current.

of the electrolyte in normality and  $V$  denotes the cataphoretic velocity multiplied by  $10^5$  as usual. Results in Table V have been obtained with sol No. 2 (*vide* Table IV) after centrifuge and those in Table VI from a sol of type A, i.e., the sol contained a moderate amount of potassium ferrocyanide. From these tables it is clear that the variation of the cataphoretic velocity with the concentration of the electrolyte depends also on the previous treatment of the sol. It is singular that in Table V, in the case of a centrifuged sol whose initial cataphoretic velocity is low, an initial rise is always observed in the cataphoretic velocity (even with the bivalent barium ion) with a gradual decrease afterwards, whereas in Table VI, with a non-centrifuged sol (containing free potassium ferrocyanide) the cataphoretic velocity first decreases and then increases with yet another drop afterwards. The sol obtained by centrifuging shows a diminution of the cataphoretic velocity in presence of an electrolyte. The higher the concentration of electrolytes taken, the greater is the effect observed.

TABLE V.

*Copper ferrocyanide hydrosol (type B).*

Electrolyte.

Electrolyte.		$\gamma$						
$C$	...	0	0.0002	0.0005	0.001	0.002	0.01	0.02
KCl		40.4	...	...	...	44.5	50.4	47.3
NaCl		40.4	...	...	...	46.4	49.9	48.5
HCl		40.4	...	...	...	42.4	44.8	40.4
BaCl <sub>2</sub>		40.4	43.4	39.4	35.4	...	...	...

TABLE VI.

*Copper ferrocyanide hydrosol (type A).*

C.	$V$			
	Potassium chloride		Sodium chloride	
	Before centrifuge.	After centrifuge.	Before centrifuge.	After centrifuge.
0	51.2	48.2	51.2	48.2
0.001	47.3	45.3	48.5	45.5
0.0025	44.5	40.2	45.5	41.5
0.025	48.4	37.2	50.2	39.2
0.05	42.4	33.4	46.2	35.2

*Effect of Dilution of the Sol in Presence and Absence of Potassium Ferrocyanide.*

It has been shown by the author (*J. Phys. Chem.*, 1928, 32, 1281) that the cataphoretic velocity of a hydrosol of copper ferrocyanide decreases on dilution. This sol was prepared by precipitating copper ferrocyanide from concentrated solutions of copper sulphate and potassium ferrocyanide. The precipitate was washed with conductivity water by decantation for about one month. Part of the precipitate peptised. It was then subjected to dialysis for about two months. A portion of this sol was diluted and measurements were taken. Another sol was prepared as stated before, but dialysis was continued for a month. The results are given in Table VII. These results suggest that the difference in the behaviour of these two types of sols is caused by the amount of potassium ferrocyanide present in the sol. Accordingly cataphoretic velocities were determined with dilution of sols, which contained initially very little free potassium ferrocyanide, in presence of increasing amounts of potassium ferrocyanide solution and the results given in Table VIII, clearly show that the behaviour of the cataphoretic velocity of the copper ferrocyanide hydrosol depends on the amount of potassium ferrocyanide initially present in the sol.

TABLE VII.

Dilution (sol : H <sub>2</sub> O) pure sol ...			1 : 1	1 : 8	1 : 7	1 : 10	1 : 81	1 : 79
V <sub>c</sub> {	Sol I ...	70.6	50.9	45.3	—	29.9	—	—
	Sol II ..	56.95	—	—	54.8	—	52	50.15

TABLE VIII.

Sol.		V at dilution of			
		Pure sol.	1 : 1	1 : 4	1 : 9
N-K <sub>4</sub> Fe(CN) <sub>6</sub> .					
I	0 c.c.	45.2	40.4	37.4	33.4
II	1	57.2	56.4	53.4	50.1
III*	10	53.4	50.4	49.3	51.4
IV*	20	45.2	40.5	46.4	44.5

\* In the U-tube, above the boundary there was formed light yellowish layer of liquid with the passage of the current indicating the migration of ferrocyanide ions above the boundary.



In Table IX are given results at different dilution of the sol in presence of varying concentrations of potassium chloride. These results show once more that when the initial cataphoretic velocity of a sol is low, the addition of electrolytes increases its value (which is sometimes followed by a decrease) depending on the amount of copper ferrocyanide present.

TABLE IX.

Dilution ratio.	V at a concentration C of KCl.				
	0	0.001	0.002	0.01	0.02
1 : 1	40.4	44.5	46.5	50.4	47.2
1 : 4	37.4	45.2	48.3	49.3	60.3

*Effect of Some Non-electrolytes on the Cataphoretic Velocity.*

Lastly the behaviour of the cataphoretic velocity of copper ferrocyanide hydrosol has been followed in presence of sugar and ethyl alcohol, as also its variation in presence of potassium chloride and barium chloride. The results given in Tables X, XI and XII have been obtained with a sol of type A (i.e., it contained a moderate amount of free potassium ferrocyanide).

TABLE X.

*Copper ferrocyanide sol, potassium chloride and ethyl alcohol.*

	V at the concentration C of KCl.							
	0	0.002	0.004	0.01	0.02	0.035	0.053	0.06
EtOH %.								
0 c.c.	54.3	...	49.3	...	...	49.5	...	40.08
2.5	50.8	...	...	41.0	...	45.6	39.1	...
10	46.1	...	...	31.8	36.1	45.3	(33.0) after coagulation	
20	41.7	35.3	34.4	30.1	...	...	...	...

Here, to start with, the initial cataphoretic velocity was high, and as usual, in presence of potassium chloride the cataphoretic velocity at first decreases, then increases with a final drop afterwards. In presence of sugar alone, the cataphoretic velocity at first decreases rapidly, but the rate of variation of the velocity with higher percentages of sugar is small. The rate of variation of the velocity with increasing concentrations of potassium chloride is smaller, the higher the percentage of sugar taken, i.e., smaller the initial cataphoretic velocity of the sol.

TABLE XI.

*Copper ferrocyanide sol, potassium chloride and sugar.*

Sugar %.	V at the concentration C of KCl.				
	0	0.004	0.0125	0.025	0.05
0 g.	54.8	49.3	46.1	49.5	40.06
2.5	44.7	...	42.7	55.7	35.6
5.0	42.0	...	41.6	44.5	32.0
10	41.7	...	39.1	40.8	The sol coagulated

TABLE XII.

*Copper ferrocyanide sol, barium chloride and sugar.*

Sugar %.	56% V	V at the concentration C of BaCl <sub>2</sub> .			
		0.0001	0.0002	0.0005	0.001
0 g.	54.8	38.9	36.2	34.8	31.0
2.5	44.7	39.55	28.1	...	20.8
5	42.8	44.3	31.05	...	23.1
10	41.8	47.8	44.1	...	The sol coagulated

With barium chloride alone, the velocity continually decreases; in presence of 2.5 % sugar, the same behaviour is observed though the initial drop is low and the final drop high compared to the velocities observed in case of barium chloride alone. In the case of 5 and 10 % sugar, we find an initial increase in the velocity of

the colloid in presence of barium chloride. In presence of ethyl alcohol alone, the cataphoretic velocity diminishes; with increasing concentrations of potassium chloride, the cataphoretic velocity at first diminishes, increases afterwards and finally there is another drop in the velocity. In the case of 20% ethyl alcohol, there is always a decrease but here of course, the velocity could not be followed up to those concentrations of electrolytes where we observe an increase in other cases.

### DISCUSSION

#### *On the Relation between Cataphoretic Velocity, Potential of the Double Layer and Density of Charge.*

Two main peculiarities are noticeable from curves in Figures 2, 4, 5, 6, and 7 in the case of uni-univalent salts in absence of non-electrolytes:

(1) First, when the initial cataphoretic velocity is low, i.e., about  $40 \times 10^{-5}$  cm. per sec. per volt per cm. there is an initial increase with a gradual drop afterwards.

(2) When the initial cataphoretic velocity is high, we get a minimum followed by a maximum or a characteristic  $\cup$  shaped curve.

FIG. 1.

*Effect of dialysis.*

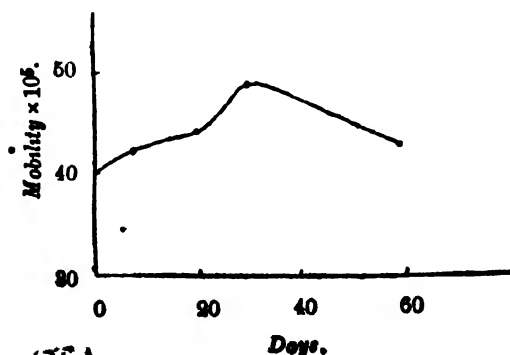


FIG. 2.

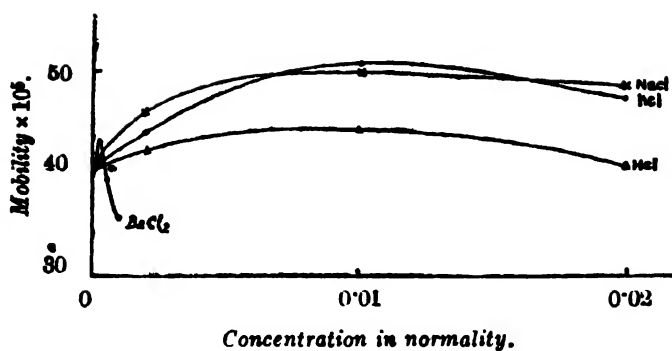


FIG. 3.

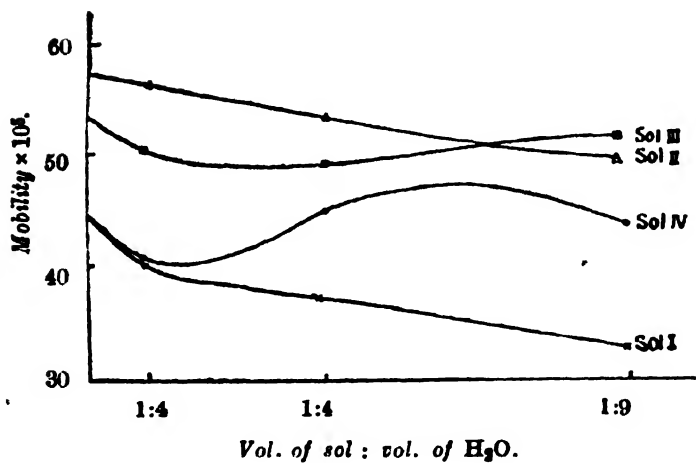
*Effect of dilution.*

FIG. 4.

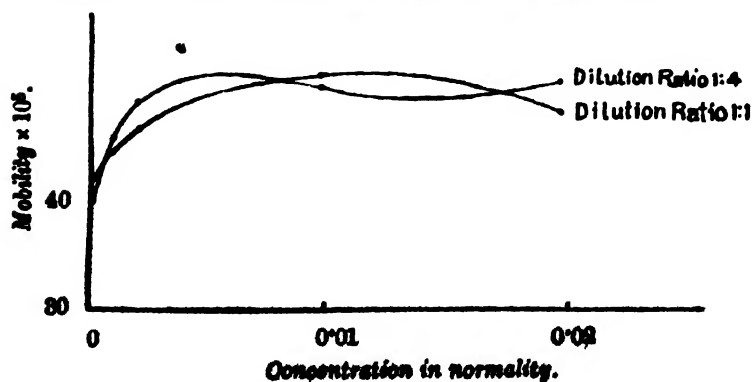
*Effect of dilution in presence of increasing conc. of KCl.*

FIG. 5.

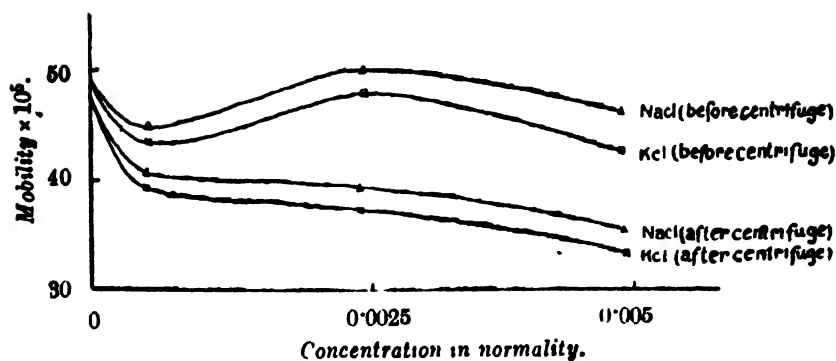


FIG. 6.

Effect of ethyl alcohol and KCl.

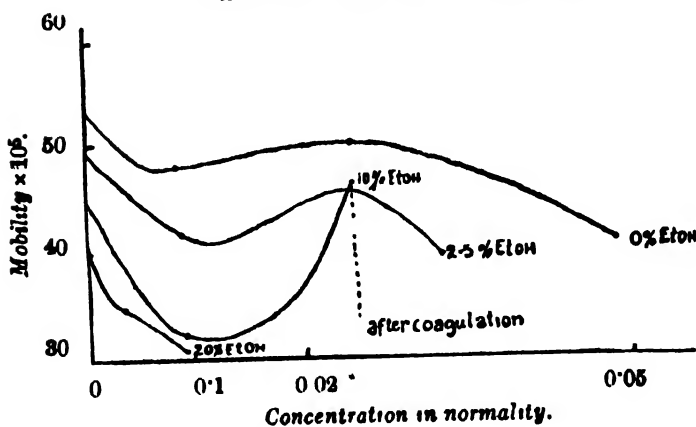


FIG. 7.

Effect of sugar and KCl.

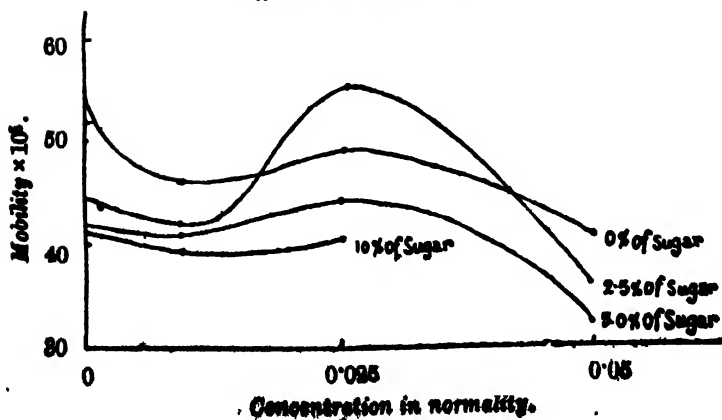
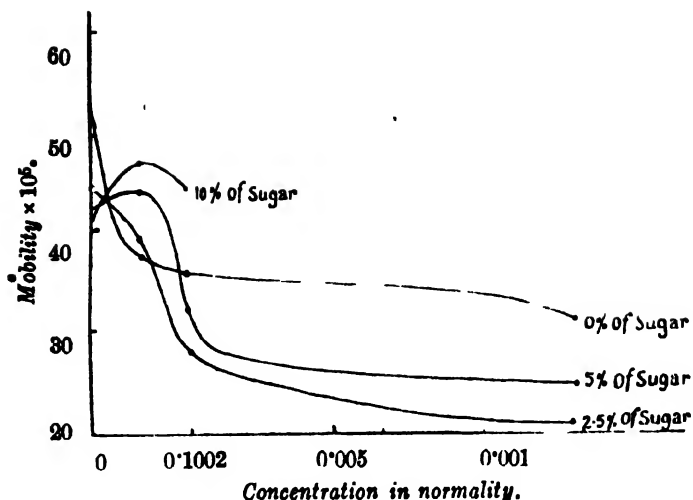


FIG. 8.

*Effect of sugar and BaCl<sub>2</sub>.*

Krulyt and Willigen (*Z. physikal. Chem.*, 1927, 139, 170), in order to explain coagulation at the high cataphoretic speeds observed in the case of uni-univalent salts, maintain that the potential is low, though the corresponding speed is high due to a higher dielectric constant. Starting from the equation,

$$\zeta = \frac{4\pi\eta u}{D} \text{ or } \zeta D = 4\pi\eta u = 4\pi U_1$$

(where  $U_1$  = the cataphoretic speed after viscosity correction,  $\zeta$  = electrokinetic potential,  $D$  = dielectric constant) they have advanced the view that the increased dielectric constant of the electrolyte is responsible for the higher cataphoretic speed observed at the high concentrations of electrolytes (uni-univalent) following the work of Furth (*Physikal. Z.*, 1920, 25, 676) and Pechhold (*Ann. Physik*, 1927, 83, 427) on the variation of the dielectric constant of solutions of electrolytes in which it was shown that the dielectric constant shows first a small decrease followed by a sharp increase afterwards as the concentration of the electrolyte is increased. It follows from their arguments that the potential of the double layer is proportional to  $U_1/D$ . The validity of this relationship can be better studied in presence of non-electrolytes alone. Now it has been already shown by Mukherjee and his coworkers (*J. Indian Chem. Soc.*, 1928, 5, 704) in the case of arsenious sulphide sol that an increase or a decrease of the dielectric constant on the addition of the non-electrolyte sometimes

produces the same effect—a lowering of the cataphoretic speed. The potential of the double layer is then apparently not determined by the change in dielectric constant alone. It is also not justified to assume a direct proportionality between density of charge and dielectric constant (*cf.* Freundlich, "Colloid and Capillary Chemistry" 1926, p. 468). Assuming that the dielectric constant of the colloidal solution changes in the same proportion as pure water with the addition of a non-electrolyte, it will be seen from the following table that the ratio of cataphoretic velocity of the colloidal copper ferrocyanide to the dielectric constant is not constant (the values  $D$ , have been obtained by interpolation from the data of Harrington, *Phys. Rev.*, 1916, 8, 581) a fact which disproves that the variation of the dielectric constant *alone* is responsible for a variation in the cataphoretic speed of the sol.

TABLE XIII.

Sugar %	0	2½	5	10
$V$	54.3	44.7	42.8	41.3
$D$	80.1	78.25	77.0	76.2
$V/D$	0.67	0.57	0.55	0.54

Further comparing the curves in presence of electrolytes in Figs. 2 and 5, it is apparent that for the same concentrations of potassium and sodium chlorides, there is observed in one case an increase and in another case a decrease in the cataphoretic velocity of the colloid. Moreover, centrifuging the sol in presence of high concentrations of electrolytes cannot evidently change the dielectric constant so much as to lower the cataphoretic velocity to such a low value as actually observed. It is also clear that the final decrease in the velocity at very high concentrations of electrolytes in some cases and the initial rise followed by a drop in others with lower concentrations cannot be explained on the basis of the change of the dielectric constant alone (*cf.* Figs. 2 and 5). These considerations show also that the observations mentioned above are not even explicable from the point of view of Kruyt and Briggs (*K. Proc. Akad. Wetensch. Amsterdam*, 1929, 32, 884), who point out that the variation of the dielectric constant in the bulk of the solution need not be considered but only that in the interface should be taken into account, in order to explain the very high cataphoretic speed observed at high concentrations of electrolytes. Moreover, this latter proposition appears to overlook the

considerations of Debye and McAulay (*Physikal. Z.*, 1925, 28, 22), who have shown that round an ion the distribution of the water molecules would not be materially altered by molecules of lower dipole moment. In other words, the dielectric constant of the water layer surrounding free charges would be materially determined by the strongest dipoles. If the argument of Debye and McAulay hold good and this appears to be obvious enough, the above explanation appears to be insufficient.

It is then obvious that the charge may be affected by other factors than dielectric constant alone. There is evidence to show that a direct relationship exists between the amount of excess of adsorption of an ion of one sign and the rate of cataphoretic movements. Lamb's equation has as its basis (*Brit. Assoc. Rep.*, 1887, p. 495), a relation connecting cataphoretic velocity and surface density of charge. An increase in the density of charge certainly denotes an increase in cataphoretic speed, since the coefficient of sliding friction changes in the same sense as the density of charge (Lamb, *loc. cit.*). In Helmholtz's treatment also the fundamental factor determining the electrical force involves the volume density of charge. From arguments due to Mukherjee (*J. Indian Chem. Soc.*, 1928, 5, 705), it appears more plausible to explain these observations by assuming that either the density of charge is changing or preferably both the density and the thickness of the double layer are changing. The great effect of cane sugar (Table XIII) points to the conclusion that the variation in the density of the charge is predominant. The interpretation of cataphoretic velocity in terms of the density of charge from the point of view of ionic equilibrium at the solid liquid interface is therefore to be preferred.

*An Explanation on the Basis of a Change of the Density of  
Charge from Mukherjee's Theory of Double Layer.*

It is, however, possible to conceive a simple picture of these processes in terms of the density of charge on the basis of the views of Mukherjee (*Trans. Faraday Soc.*, 1921, 16, 108) on the nature of double layer. A colloidal particle in its process of formation adsorbs chemically a certain species of ions on its surface and thus acquires its charge. In consequence of the charge, ions of opposite sign will be drawn near the surface—some of which are bound and some are free depending on the kinetic energy of these ions. The charge, imparted to the colloidal particle is due to the number of primary ions still remaining ;



uncovered. Now it is clear that just as the primarily adsorbed ions exert forces of attraction on the oppositely charged ions in the liquid to get them fixed or bound to the surface, so ions in the liquid similarly charged to that of the colloid exert an attractive force on these bound ions and try to pull them towards the interior of the solution. Whether an ion will be bound or not will depend on the relative magnitudes of these two opposing forces. The origin of the charge of the colloidal copper ferrocyanide is usually ascribed to the preferential chemical adsorption of ferrocyanide ions during the process of formation of the colloid. The cataphoretic velocity or the density of charge will be low,

Firstly (1) when the colloid initially contains traces of potassium ferrocyanide (i.e., ferrocyanide ions) and therefore adsorbs chemically only a few ferrocyanide ions per unit surface of the colloidal particle, in consequence, a large number of places on the surface of the particles where ferrocyanide ions could be chemically adsorbed are vacant and hence the surface of the colloidal particles might be said to be "unsaturated." These conditions are realised in a sol of type B.

(2) Secondly either, (a) when the sol contains very high concentrations of potassium ferrocyanide (before dialysis, cf. Fig. 1), or (b) by increasing either only the number (with the addition of a non-electrolyte of low dielectric constant, cf. Figs. 6, 7, 8 or with the addition of potassium salts) or both the number and valency (with the addition of other electrolytes) of the bound ions when the sol initially contains moderate amounts of potassium ferrocyanide (initial cataphoretic velocity high—a sol of Type A), i.e., when the surface of the colloidal particles had almost been "saturated" due to the primary adsorption of ferrocyanide ions

#### *Variation of the Charge with Simple Electrolytes.*

In both the cases mentioned above when the initial density of charge is low, the number of similarly charged ions that can approach near about the interface will be comparatively high and that of the oppositely charged ions will be relatively low, and thus there is a greater probability of initial increment of charge [in case (1) due to the primary chemical adsorption of similarly charged ions and in case (2) owing to the removal of bound ions as a result of attraction towards the interior of the liquid by the

similarly charged ions to that of the colloid]. If the initial cataphoretic velocity is low due to condition (1) as in a sol of type B where traces of potassium ferrocyanide are present, low concentrations of electrolytes (specially uni-univalent salts) will increase the charge due to the primary chemical adsorption of negatively charged ions as the surface of the particles are unsaturated (here chlorine ions; see Figs. 2 and 4). With increasing concentrations of electrolytes as the charge tends to be higher and higher, more oppositely charged ions are attracted and similarly charged ions repelled with the result that at higher concentrations of electrolytes the cataphoretic velocity diminishes again. With very low concentrations of barium chloride there is an initial increase in the density of charge; thus even the bivalency of barium is not sufficient to counteract the primary chemical adsorption of chlorine ions, perhaps because of the tetravalency of the primarily adsorbed ions. Had the primarily adsorbed ion been monovalent, there would have been less chance of observing this increment in charge with a bivalent cation. Subsequently however the drop is much steeper as is to be expected (*cf.* Fig. 2).

When the initial density of charge (*i.e.*, cataphoretic velocity) is high (curves obtained without centrifuge and 0% non-electrolyte in Figs. 5—7,—these sols were of type A which contained moderate amounts of free potassium ferrocyanide), obviously there will be at first a diminution as more of the oppositely charged ions will be attracted; but as the charge becomes lower, the number of similarly charged ions will be comparatively greater near about the surface and exert their influence in removing the bound ions (primary chemical adsorption of anions is less probable here, first because of "saturation" of the surface due to the primary adsorption of ferrocyanide ions and secondly because of attractive forces exerted on them when they pass through a layer of oppositely charged bound ions and repulsive forces due to primarily adsorbed ferrocyanide ions) resulting in actual increment of charge at these high concentrations of electrolytes. It is to be noted that appreciable coagulation has taken place at these concentrations of electrolytes and smaller particles are combining to form larger aggregates in which process the mutual repulsive forces between the bound ions themselves will be brought into play. Moreover, the change in the curvature resulting from aggregation may also modify the charge (Alty, *Proc. Roy. Soc.*, 1924, 106, 1). It is therefore to be expected that in this

region of coagulation when by centrifuging the larger aggregates are thrown down and separated, the cataphoretic velocity acquires a low value (Fig. 5). As the density of charge tends to be high, a greater number of oppositely charged ions will be attracted and thus there will be observed a final decrease. With barium chloride the first diminution is very sharp, but as the density of charge tends to be low, the effect of similarly charged ions comes into play with the result that at higher concentrations, the curve is almost flattened (Fig. 8, 0% sugar). No increment is observed here at the coagulating concentrations probably because of the higher valency of the barium ion.

#### *Variation of the Charge with Dialysis and Dilution*

It is not difficult also to understand the nature of the curves (Figs. 1 and 8) obtained on dialysis and on dilution in presence of potassium ferrocyanide. On dialysis with decrease in the concentration of potassium ferrocyanide first the number of bound potassium ions decreases, thus increasing the density of charge and therefore the cataphoretic velocity. When the concentration of potassium ferrocyanide becomes appreciably low, it is conceivable that there occurs a decrease in the number of the primarily adsorbed ferrocyanide ions, so that finally there is a decrease in the cataphoretic velocity. On dilution of the sol in absence of potassium ferrocyanide, the cataphoretic velocity decreases thus showing a diminution in the number of primarily adsorbed ferrocyanide ions; in presence of small concentrations of potassium ferrocyanide, the density of charge diminishes but not so markedly as in its absence, for here the decrease in the number of primarily adsorbed ferrocyanide ions cannot be so marked due to the presence of greater number of ferrocyanide ions. With sol III, there is at first a decrease with an increase afterwards while with sol IV, in addition to this there is a final decrease though not so prominent. With dilution as the cataphoretic velocity tends to be low, the number of ferrocyanide ions (for the concentration of potassium ferrocyanide is high) that can approach near enough the surface also increases with the result that the velocity afterwards increases again. The final decrease shows that as the density of charge increases, more oppositely charged ions are attracted and adsorbed as bound ions.

*Variation of the Charge with Non-electrolytes.*

The effect of non-electrolytes can also be understood from the above standpoint in a general way. Addition of pure non-electrolytes will decrease the dielectric constant of the medium and thus depress also the cataphoretic velocity due to the increase in the number of bound ions (Figs. 6—8, sols of type A). The activities of the ions present will also change due to a change in the dielectric constant with the addition of a non-electrolyte (Debye and Hückel, *Physikal. Z.*, 1923, **24**, 305, 365). Recent researches on the activity coefficients of ions in aqueous solutions of non-electrolytes by Brönsted and Williams (*J. Amer. Chem. Soc.*, 1928, **50**, 1338), Hansan and Williams (*ibid.*, 1930, **52**, 2759), and others (Lucasse, *ibid.*, 1926, **48**, 323; Scatchard, *ibid.*, 1927, **49**, 217) have in general shown the quantitative verification of the theory of Debye and Hückel in very dilute solutions of electrolytes. In the following (where high concentrations of electrolytes are generally used) it is sufficient to know in a qualitative way that as the dielectric constant decreases the activity coefficient and therefore the activity of ions also decreases. It is seen (Fig. 8) that at 2½% sugar, an initial rise is not observed in the velocity as barium is bivalent and is thus probably able to compensate for the increased number of similarly charged ions that can approach near enough the double layer. In this connection the difference between the removal of bound ions and the chemical adsorption of primarily adsorbed ions is to be noted, both resulting in an increment of charge (*cf.* also Fig. 2). The density of charge is a little higher in presence of 2½% sugar ( $44.7 \times 10^{-5}$  cm. per sec. per volt per cm. as compared to 40.4 expressed in the same units in Table V, Fig. 2). This may perhaps account for the absence of initial increment here. From 2½% to 5 and 10% sugar, the number of bound ions available for removal is higher, as is evidenced by the low cataphoretic velocity. Comparing the results with 5% and 10% sugar, it is seen that the initial rise in the velocity is higher in the case of 10% sugar. Though both the number of similarly charged ions that can approach near enough the surface and the number of bound ions are slightly higher at 10% sugar solution and may account for the higher initial rise, it is better to keep in view in this case the variation in another factor, namely, in the activity of the barium and chlorine ions with the addition of sugar. In considering this variation, it is to be borne in mind that for each barium ion, there are two chlorine ions and it is possible that the activities of these

ions may change due to the formation of some  $\text{BaCl}$  and  $\text{Cl}$  ions in addition to the change in the dielectric constant. In this way the proportionate decrease in the concentration of free barium ions (and therefore in the activity) would be greater than that in the number (and activity) of free chlorine ions, and this effect would be greater, the higher the percentage of sugar taken. That some such consideration is necessary would appear also from the results obtained with this sol and potassium chloride in presence of sugar (*vide* Fig 8, sol of type A). At a higher concentration of the electrolyte, the rise is most marked, though it gradually diminishes with higher percentages of sugar. Considering individually the curve at a particular percentage of sugar, the results are explicable as they show the usual decrease with increase afterwards and a final drop in the velocity, except in the case of 10% sugar where measurements could not be proceeded with high concentrations of electrolyte due to coagulation. The curves however tend to be more and more flattened at lower concentrations of the electrolytes, and the first lowering becomes less and less pronounced as higher percentages of sugar are taken. With even 10% sugar (when the cataphoretic velocity is  $41.3 \times 10^{-5}$  cm. per sec. per volt per cm.) and 0.125N-KCl there is no increment. The activities of potassium and chlorine ions are expected to be diminished in the same proportion so that for a particular percentage of sugar unless the concentration of free chlorine ions (*i.e.*, potassium chloride) is high, a rise in the charge is not observed (*cf.* with  $\text{BaCl}_2$ ). Thus it appears that when the surface of the colloidal particle remains saturated (due to the adsorption of maximum number of primarily adsorbed ions) the initial increment in the charge may not be observed even if the density of the charge is low. Hence, the effect of the primary chemical adsorption of similarly charged ions in increasing the charge is seen to be more pronounced than that of the removal of bound ions when other factors such as activities of ions as in the case of barium chloride do not interfere. It is to be noticed that at 0.025N potassium chloride, the velocity shows an increase in absence of sugar; if  $2\frac{1}{2}\%$  sugar is added, the rise also is most prominent, as here the number of similarly charged ions increases greatly (since by addition of  $2\frac{1}{2}\%$  sugar alone, the drop in the velocity is high, *i.e.*, from  $54.8 \times 10^{-5}$  to  $44.7 \times 10^{-5}$  cm. per sec. per volt per cm.) but the diminution in the activity of potassium ions is expected to be less, compared to that in the case of higher percentages of sugar.

A relatively greater diminution in the activity of potassium ions combined with higher attractive forces for oppositely charged ions and greater repulsive forces for similarly charged ions due to a greater lowering of the dielectric constants perhaps account for the diminution in charge at higher percentages of sugar in presence of 0.025N-potassium chloride.

It is noteworthy that with ethyl alcohol (Fig. 6) and potassium chloride the results are not exactly similar to those in presence of sugar. With ethyl alcohol alone, the density of charge is not so much diminished as in the case of sugar, showing that the number of bound ions (here potassium ions from free potassium ferrocyanide in the chloride) does not increase so much due probably to the comparatively lower activity of potassium ions in presence of ethyl alcohol on account of a greater diminution of the dielectric constant. Moreover, the great diminution of the mobility of potassium ions in presence of ethyl alcohol (Ulich, *Trans. Faraday Soc.*, 1927, 23, 390) is possibly also to a certain extent responsible for this behaviour of the colloid. Curves with 0% and 2.5% ethyl alcohol in Fig 6 separately considered show the usual  $\Lambda$ -shape as the density of charge is initially high. Curve with 10% ethyl alcohol shows first a decrease with an increase afterwards, whereas that with 20% ethyl alcohol shows always a decrease, for in these two cases experiments could not be proceeded with due to coagulation setting in. Ethyl alcohol decreases the dielectric constant more than sugar and also the initial density of charge, to start with, was higher except in the case of 20% ethyl alcohol; so that the force with which the oppositely charged ions are bound and similarly charged ions repelled in this medium is stronger with the result that there is not only no increment, but on the other hand it is seen that the rate of initial diminution of the cataphoretic velocity of the colloidal copper ferrocyanide with concentration of potassium chloride is higher, the higher the amount of alcohol taken. With higher concentration of electrolytes the subsequent rise is also higher, the higher the percentage of alcohol taken except in the case of 20% alcohol where it is not possible to measure the velocity at these concentrations of electrolytes. In the case of 10% ethyl alcohol the colloid after partial coagulation shows a lower density of charge. This is also easily explicable from the point of view developed above. In the case of 20% ethyl alcohol, though the initial density of charge is low, there is no initial rise obviously due to the very great lowering of

dielectric constant, with the result that the similarly charged ions are repelled and the oppositely charged ions are bound with a comparatively much higher force. Thus all these considerations show that only under certain conditions, an initial increment in the charge is possible. Possibly besides the change in the dielectric constant of the medium and the activities of ions with the addition of these non-electrolytes, there is also a variation in the thickness of the double layer, in the mobilities and the apparent radii of the ions concerned—but our knowledge about these properties is not sufficient to warrant discussions on such a basis in detail.

#### CONCLUSION.

In this paper an attempt has been made to explain the different types of results on cataphoretic velocity, in presence of electrolytes and non-electrolytes essentially on the basis of the double layer as conceived by Mukherjee (*loc. cit.*). While these considerations are sufficient to indicate at least qualitatively the nature of the curves showing the variation in the cataphoretic velocity of a colloid in presence of electrolytes and non-electrolytes it is realised that in view of the absence of relevant data on the dielectric constant of mixtures of electrolytes, colloids and non-electrolytes, any quantitative explanation is not possible. But though limited in this way, it has been shown (on the assumption of a proportionate variation in the dielectric constant of the colloid as that of water on the addition of a non-electrolyte) by taking into consideration other factors than dielectric constant, that an initial rise in the cataphoretic velocity of colloids is possible even without the chemical adsorption of similarly charged ions or any increase in the dielectric constant (*cf.* Fig. 8 with  $\text{BaCl}_2$ ). A strong possibility has also been pointed out that increment of cataphoretic velocity of a colloid does not always indicate an increment of charge due to the chemical adsorption of ions similarly charged to that of the colloid. From these considerations it is also possible to conceive a simple mechanism of the displacement of a bivalent ion by a monovalent ion or of cationic antagonism in the case of negatively charged hydrosols (the cataphoretic velocity is increased with the addition of a salt with monovalent precipitating ion when the density of the charge has already been diminished by a salt with bivalent precipitating ion as observed by Mukherjee, Chaudhury and Raichaudhury, and the

increment ascribed to the displacement of a bivalent ion, *J. Indian Chem. Soc.*, 1927, 4, 493). All these results on the cataphoretic velocities and particularly those near about the coagulating concentrations of electrolytes and their interpretations show that it is not now possible to think of coagulation taking place at a critical potential both from the theoretical and experimental points of view, and that equicoagulating concentrations of electrolytes do not always depress the charge of the colloidal particle to the same extent and that the adsorbability and the coagulating power of a precipitating ion cannot always go hand in hand, as first pointed out by Wo. Ostwald (*Kolloid Z.*, 1920, 26, 28)

My best thanks are due to Prof J N Mukherjee, D Sc, for guidance and helpful criticism and to Lt. Col R N. Chopra M.A., M.D. (Cantab.), I.M S., Professor of Pharmacology and Officiating Director of School of Tropical Medicine for his kind encouragement and sympathy during the course of this investigation. Thanks are also due to my friend Mr N. P Chatterjee, M.Sc, without whose invaluable help most of the observations with non-electrolytes could not have been taken.

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## Photosynthesis of Nitrogenous Compounds.

By L. N. BHARGAVA AND N. R. DHAR.

In a series of papers Baudisch (*Ber*, 1911, **44**, 1009; 1913, **46**, 115; 1917, **50**, 652) first investigated *in vitro* the photo-formation of nitrogenous compounds by exposing a mixture of formaldehyde and potassium nitrate or nitrite to radiations from a mercury vapour lamp. Instead of formaldehyde, he sometimes used methyl alcohol. He reported the formation of formhydroxamic acid and its potassium salts in his experiments, and an alkaloidal substance was also obtained but he could not identify it as the amount was exceedingly small. He seemed to have also obtained pyrrol and pyridine derivatives in very small quantities.

Baly, Heilbron and Stern (*J Chem. Soc.*, 1923, **123**, 165), after exposing ammonia solutions, saturated with carbon dioxide to radiations from a quartz-mercury vapour lamp, seemed to have obtained methylamine and pyridine. According to Baly and co-workers, if ammoniacal solutions of cupric carbonate saturated with carbon dioxide are used, methylamine and pyridine or piperidine are formed. When 2M solutions of formaldehyde and ammonia are exposed to ultraviolet light from 6 to 10 days, a solid brown substance giving the reactions of the alkaloid coniine is reported to be formed along with other products already mentioned. Snow and Stone (*ibid.*, 1923, **123**, 1509), however, have stated that the evidence of Baly, Heilbron and Stern (*loc cit.*) for the formation of pyridine and coniine is inconclusive.

Dhar and Sanyal (*J. Phys. Chem.*, 1925, **29**, 926), by exposing ammonia, carbonic acid and formaldehyde for 20 hours to sunlight, could obtain methylamine but no pyridine. On exposing ammonia, formaldehyde and cupric carbonate for 80 hours to tropical sunlight, they obtained methylamine and an alkaloidal substance the identity of which could not be established as the amount was small.

It will be evident, therefore, that some complex nitrogenous substances have been obtained by the action of light on a mixture of formaldehyde and nitrite or ammonia in presence of catalysts. But the amounts being exceedingly small, the results are not very definite.

and not exactly reproducible. Moreover, the view has been advanced that the synthesis of proteins can take place in the dark provided carbohydrate is available and that the nitrogen assimilation is not a photochemical process.

In view of this unsatisfactory position of the problem of the photosynthesis of nitrogenous compounds, a systematic work on this line has been undertaken in this laboratory. In this communication, we are recording our results obtained on the photosynthesis of methylamine and nicotine, on exposing formaldehyde and ammonia with different catalysts to tropical sunlight.

#### EXPERIMENTAL.

2% Solutions of Merck's formaldehyde after distillation were mixed with small amounts of concentrated ammonia and were exposed to sunlight for a long time in presence of different catalysts, *e.g.*, zinc oxide, titanium oxide, copper carbonate, nickel carbonate, etc. After the necessary exposure, the solutions were filtered and distilled over a sand-bath. The amine was tested for in the distillate. The residue left in the flask was treated with ether. The ether extract was shaken with dilute sulphuric acid. If any basic substance were present, it would come in the aqueous layer, which was made alkaline and again shaken with ether. In our experiments, the second ethereal extract was very small and it smelt like tobacco. Hence, we suspected the presence of nicotine but as a large amount of hexamethylenetetramine is also formed by the action of ammonia and formaldehyde and as this substance showed all the tests of alkaloids, precautions were taken to remove hexamethylenetetramine from the mixture. We have observed that the precipitate obtained by the addition of mercuric chloride solution to hexamethylenetetramine is white but the precipitate with nicotine is yellow, which dissolves readily in dilute acetic acid, but the white precipitate obtained from hexamethylenetetramine and mercuric chloride is not readily soluble in dilute acetic acid. This is how we could separate a small quantity of nicotine from hexamethylenetetramine.

In order to find out whether any nitrogenous compound is formed in the absence of light, blank experiments with the reacting substances and catalysts in the same proportions were carried on in vessels kept in the dark for the same period as in light. The reacting substances kept in the dark were also analysed according to the

method already mentioned, but in no case could we detect the presence of methylamine or any nitrogenous compound except hexamethylenetetramine.

TABLE I.

Experiment.	Time of exposure to sunlight.	Results.
1. 2% Formaldehyde (150 c.c.) and 6.2 <i>N</i> -ammonia (6 c.c.) and cupric carbonate (6 g.) in three sealed bulbs	80 hr.	Hexamethylenetetramine, methylamine and nicotine obtained
2. 2% Formaldehyde (500 c.c.) and 6.2 <i>N</i> -ammonia (15 c.c.) and cupric carbonate (5 g.) in two pyrex glass beakers	120	Hexamethylenetetramine, methylamine and an oily substance of nicotine smell obtained
3. 2% Formaldehyde (500 c.c.) and 6.2 <i>N</i> -ammonia (10 c.c.) and cupric carbonate (5 g.) in a glass trough	110	Hexamethylenetetramine, methylamine and nicotine obtained
4. 2% Formaldehyde (200 c.c.) and 6.2 <i>N</i> -ammonia (4 c.c.) and titanium oxide (4 g.) in three sealed bulbs	80	Do
5. 2% Formaldehyde (2000 c.c.) and 6.2 <i>N</i> -ammonia (25 c.c.) and titanium oxide (5 g.) in a big enameled dish	120	Do
6. 2% Formaldehyde (2000 c.c.) and 6.2 <i>N</i> -ammonia (25 c.c.) and titanium oxide (5 g.) in a big enameled dish	130	Do
7. 2% Formaldehyde (500 c.c.) and 6.2 <i>N</i> -ammonia (10 c.c.) and zinc oxide (5 g.) in a glass trough	90	Do
8. 2% Formaldehyde (2000 c.c.) and 6.2 <i>N</i> -ammonia (25 c.c.) and zinc oxide (5 g.) in a big enameled dish	130	Do

The nicotine was obtained as the hydrochloride and all the standard tests were applied. In order to be definite that the substance obtained is practically pure nicotine hydrochloride, we determined the molecular weight by igniting known weights of the dry chloroplatinate of the base and the following values of the molecular weights were obtained.

TABLE. II.

Chloroplatinate.	Platinum obtained.	M. W. found.	Actual M. W. of nicotine.
1. 0.0041 g	0.0011 g.	158.68	162.18
2. 0.0569	0.0152	160.25	
3. 0.0612	0.0163	161.35	

It appears, therefore, that we have been able to obtain nicotine practically in a pure condition by exposing formaldehyde and ammonia with catalysts like cupric carbonate, titanium oxide, zinc oxide etc., for a long time to sunlight. But cupric carbonate seems to be the best catalyst.

In most preparations, after filtering the solution and distilling the filtrate, methylamine was obtained. Methylamine could be detected by the carbylamine test and by the melting point of the hydrochloride.

We are of the opinion that in the photosynthesis of nitrogenous compounds, in order to get positive evidence, the following points should be noted :

(a) The temperature of the reacting mixture may not exceed 35°. (b) Better yield of the nitrogenous compound is obtained if the incident radiation is rich in ultraviolet radiations. (c) The intensity of the light must be high.

We carried on some experiments with a mercury vapour lamp and after an exposure lasting for 25 hours, a mixture of 2% formaldehyde (500 c. c.) and 10 c. c. of 6 *N*-ammonia without any photocatalysts yielded methylamine and nicotine.

#### DISCUSSION.

From the researches carried on in these laboratories, we are of the opinion that formaldehyde is actually formed from carbon dioxide and water vapour by the absorption of light. In a recent communication Dhar and Atma Ram (*J. Indian Chem. Soc.*, 1933, 10, 287) have reported that from 0.001 to 0.00015 g. of formaldehyde is present per litre of freshly collected rain-water and they have attributed the presence of formaldehyde in rain-water to its photo-formation from carbon dioxide and water vapour present in the atmosphere. Moreover, the above authors (*Z. anorg. Chem.*, 1932, 206, 171) have obtained larger yields of formaldehyde by the photo-reduction of

carbonic acid and bicarbonates by metals like cerium, magnesium, etc. Also there is the possibility of the generation of formaldehyde by the photo-decomposition of carbohydrates, organic acids and other organic substances. It is well known that ammonia and its compounds occur in the atmosphere and these are washed down to the soil by rain-water. In recent communications (Rao and Dhar, *Soil Science*, 1931, 31, 379; *Z. anorg. Chem.*, 1931, 199, 422) it has been shown that ammonia and its compounds present in the atmosphere and in the soil are converted into nitrite by their oxidation by air in presence of sunlight. Hence, in nature, formaldehyde and nitrite or ammonium salts react forming the basis of complex nitrogenous substances. Also the sugars present in the plants may undergo partial oxidation to mucic acid. It has already been stated that some investigators have reported the formation of pyridine on exposing a mixture of formaldehyde and nitrite or ammonia solutions. It seems likely that pyridine derivatives of the nature of  $\beta$ -aminopyridine may also be formed by the condensation of methylamine and formaldehyde. The mucic acid and the  $\beta$ -aminopyridine may form nicotine passing through different stages.

It is interesting to note that Pictet, and Rotschy (*Ber.*, 1904, 37, 1225) have already synthesised *laevo*-nicotine corresponding to the natural alkaloid starting from  $\beta$ -aminopyridine and mucic acid in the laboratory in the absence of light.

Attempts are being made to find out whether the photosynthesised nicotine is optically active or not. The photosynthesis of other nitrogenous compounds is in progress.

As no nicotine or methylamine could be obtained by keeping the reacting substances in the same proportions in the dark under conditions similar to those kept in the light, we believe that light is essential for the formation of methylamine and nicotine from formaldehyde and ammonia. It appears, therefore, that the view that the synthesis of complex nitrogenous compounds is not photochemical in nature, is incorrect.

#### SUMMARY.

1. By exposing 2% solutions of formaldehyde and small quantities of ammonia in presence of catalysts, e.g., copper carbonate, zinc oxide, titanium oxide, etc., to sunlight or to radiations from a mercury vapour lamp, methylamine and nicotine have been obtained.

2. Nicotine can be separated from hexamethylenetetramine, which is always obtained in large quantity in these reactions by the solvent action of dilute acetic acid on the yellow derivative obtained with solutions of mercuric chloride and nicotine. This derivative of nicotine dissolves readily in dilute acetic acid solutions, whilst the hexamethylenetetramine compound obtained with mercuric chloride is white and is insoluble in dilute acetic acid.

3. The molecular weight of the photosynthesised nicotine was determined by igniting known weights of the chloroplatinate of the base and weighing the platinum. The mean value of the molecular weight of the nicotine obtained by photosynthesis is 160.09 and theory requires 162.13.

4. A probable mechanism for the formation of nicotine in light seems to be the condensation of  $\beta$ -aminopyridine with mucic acid.

5. It appears from our results that the synthesis of nicotine from formaldehyde and nitrite or ammonia requires light and the view that the synthesis of nitrogenous compounds in nature is not photochemical seems to be incorrect.

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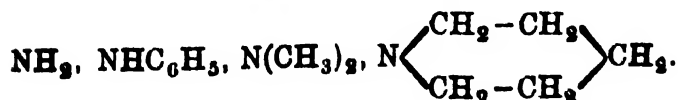
*Received January 20, 1933.*

# On some Dinitropolyhalogen Derivatives of Benzene.

BY SHIAM SUNDAR JOSHI AND SHRIRANG M. SANE.

It has been shown in earlier papers (*J. Chem. Soc.*, 1924, 123, 2481; *J. Indian Chem. Soc.*, 1928, 5, 299; 1932, 9, 59) that the action of *p*-toluenesulphonyl chloride on dinitrophenols first observed by Ullmann and Nadai (*Ber.*, 1908, 41, 1870) provides one of the best and readiest methods of replacing a hydroxyl group by a chlorine atom, and if suitable derivatives of benzene containing a hydroxyl group are selected, chloroderivatives of these compounds are obtained containing the chlorine atom in a known position. The chlorine atom so introduced is very labile and is capable of being replaced by various groups. A large number of these chloro derivatives have already been described (*loc. cit.*) and it is proposed in this paper to further characterise them by describing a certain number of derivatives obtained from each.

It is well known that a chlorine atom having two nitro groups in the 2:4 or 2:6 position is very reactive. The reactivity of the halogen atoms in the following four compounds has been studied: 1-chloro-4-bromo-2:6-dinitrobenzene, 1-chloro-4-iodo-2:6 dinitrobenzene, 1-chloro-2-bromo-4:6-dinitrobenzene, 1-chloro-2-iodo-4:6-dinitrobenzene. It has been found that the chlorine atom in each of the above compounds can be directly replaced by the following groups:



These compounds readily react with *p*-phenylenediamine giving rise to diphenyl-*p*-phenylenediamine derivatives. They readily condense with phenylhydrazine forming triazoles. They also react with *o*-aminophenol, a phenoxazine being the product of the reaction.

## EXPERIMENTAL.

*Derivatives from 1-Chloro-4-bromo-2:6-dinitrobenzene.*

**4-Bromo-2:6-dinitroaniline** was obtained by passing a current of ammonia into a boiling alcoholic solution of 1-chloro-4-bromo-2:6-dinitrobenzene (2.8 g.). The liquid soon became reddish; after half an hour the current of ammonia was stopped and the liquid cooled and filtered and the bromodinitroaniline crystallised from alcohol in orange needles, m.p.  $159^{\circ}$  (cf. Meldola and Streatfield, *J. Chem. Soc.*, 1898, 73, 688; see also *Ber.*, 1876, 9, 919). (Found: N, 16.01. Calc.: N, 16.04 per cent).

**4-Bromo-2:6-dinitrodiphenylamine**.—A solution of 1-chloro-4-bromo-2:6-dinitrobenzene (2.8 g.) in alcohol was heated on the water bath with aniline (2 c.c.). The liquid soon turned red and on cooling the diphenylamine derivative separated out after half an hour and was crystallised from alcohol in orange needles, m.p.  $122^{\circ}$ , yield 3 g. (Austen, *Ber.*, 1876, 9, 920) (Found: N, 12.15. Calc.: N, 12.43 per cent).

**4-Bromo-2:6-dinitrodimethylaniline**.—To an alcoholic solution of 1-chloro-4-bromo-2:6-dinitrobenzene (2.8 g.) dimethylamine (38%, 4 c.c.) was added and the mixture boiled on the water-bath for half an hour. On cooling orange-yellow plates separated out (2.3 g.) which were recrystallised from alcohol or from a mixture of acetone and water, m.p.  $119^{\circ}$ . (Found: N, 14.58.  $C_8H_8O_4N_2Br$  requires N, 14.48 per cent).

**4-Bromo-2:6-dinitrodiphenylpiperidine**.—Piperidine (2 c.c.) was added to a solution of 1-chloro-4-bromo-2:6-dinitrobenzene (2.8 g.) in alcohol and the mixture kept on the boiling water-bath for half an hour; an orange compound separated out on adding some water and cooling; orange yellow needles from dilute alcohol and also from dilute acetic acid, m.p.  $110^{\circ}$ , yield 2.9 g. (Found: N, 12.46.  $C_{11}H_{12}O_4N_3Br$  requires N, 12.78 per cent).

**Dibromotetranitrodiphenyl-p-phenylenediamine**.—A solution of 1-chloro-4-bromo-2:6-dinitrobenzene (2.8 g.) in alcohol, *p*-phenylenediamine (0.6 g.) and anhydrous sodium acetate (3 g.) were heated on a boiling water-bath. The liquid soon darkened and dark crystals began to separate. After about 45 minutes the liquid was cooled and filtered. The *p*-phenylenediamine derivative dissolves sparingly in alcohol and acetone and moderately in acetic acid and crystallises



from an excess of acetic acid in dark red crystals, m.p. above  $800^{\circ}$ , yield 2.6 g. (Found: N, 18.79.  $C_{10}H_8O_2N_2Br_2$  requires N, 14.05 per cent).

**8-Bromo-5-nitrophenoxazine.**—1-Chloro-4-bromo-2:6-dinitrobenzene (2.8 g.) dissolved in alcohol, *o*-aminophenol (1.2 g.) and anhydrous sodium acetate (3 g.) were heated on a boiling water-bath. The liquid soon became dark and crystals began to separate. After about an hour the liquid was cooled and filtered. The phenoxazine dissolves sparingly in alcohol and moderately in acetic acid and crystallises from acetic acid in violet silky needles, m.p.  $179^{\circ}$ , yield 1.4 g. (Found: N, 8.83; Br, 26.0.  $C_{12}H_7O_3N_2Br$  requires N, 9.12; Br, 26.04 per cent).

**2-Phenyl-5-bromo-7-nitropseudoaziminobenzene.**—A solution of 1-chloro-4-bromo-2:6-dinitrobenzene (2.8 g.) in alcohol and phenylhydrazine (2.1 g.) were heated together on a water-bath. Soon after shining crystals began to separate. The liquid was cooled after half an hour and filtered. The compound dissolves sparingly in alcohol and in acetone and crystallises from toluene in beautiful shining golden yellow plates, m.p.  $199^{\circ}$ , yield 2.8 g. (Found: N, 17.68.  $C_{12}H_7O_2N_4Br$  requires N, 17.55 per cent).

Derivatives from other compounds containing a labile chlorine atom can be obtained in the manner described above and they are briefly described.

#### *Derivatives from 1-Chloro-4-iodo-2:6-dinitrobenzene.*

**4-Iodo-2:6-dinitroaniline** dissolves slightly in alcohol, easily in acetone, acetic acid and toluene. It crystallises from alcohol in orange silky needles, m.p.  $175^{\circ}$ . (Found: N, 13.42.  $C_6H_4O_4N_3I$  requires N, 13.60 per cent).

**4-Iodo-2:6-dinitrodimethylaniline** dissolves easily in common organic solvents and crystallises from alcohol in orange silky needles, m. p.  $100^{\circ}$ . (Found: N, 12.27.  $C_8H_8O_4N_3I$  requires N, 12.47 per cent).

**4-Iodo-2:6-dinitrodiphenylamine** dissolves easily in common organic solvents and crystallises from alcohol in dark red plates, m. p.  $185^{\circ}$ . (Found: N, 10.85.  $C_{12}H_8O_4N_3I$  requires N, 10.92 per cent).

**4-Iodo-2:6-dinitrophenylpiperidine** dissolves sparingly in alcohol and easily in acetone and crystallises from a mixture of alcohol and

acetone in yellow crystals, m.p. 99°. (Found: N, 11.17.  $C_{11}H_{12}O_4N_3I$  requires N, 11.15 per cent).

*3-Iodo-5-nitrophenoxazine* dissolves very sparingly in alcohol and acetone and benzene. It crystallises from acetic acid in violet silky needles, m. p. 210°. (Found: N, 7.8.  $C_{12}H_7O_3N_2I$  requires N, 7.91 per cent).

*2-Phenyl-5-iodo-7-nitropseudoaziminobenzene* dissolves easily in alcohol and toluene and crystallises from toluene in yellow crystals, m. p. 209°. (Found: N, 15.06.  $C_{12}H_7O_2N_4I$  requires N, 15.30 per cent).

#### *Derivatives from 1-Chloro-2-bromo-4:6-dinitrobenzene*

*2-Bromo-4:6-dinitrophenylpiperidine* dissolves easily in common organic solvents. It crystallises from alcohol and also from a mixture of acetone and water in shining golden plates, m. p. 127° (Found: N, 12.54.  $C_{11}H_{12}O_4N_3Br$  requires N, 12.73 per cent).

*2-Phenyl-7-bromo-5-nitropseudoaziminobenzene* dissolves very slightly in alcohol, slightly in acetone and more easily in toluene. It crystallises from toluene in shining colourless crystals, m. p. 174°. (Found: N, 17.78; Br, 25.23.  $C_{12}H_7O_2N_4Br$  requires N, 17.55; Br, 25.08 per cent)

Some other derivatives of 1-chloro-2-bromo-4:6-dinitrobenzene have already been described (*J. Chem. Soc.*, 1924, 125, 2481).

#### *Derivatives from 1-Chloro-2-iodo-4:6-dinitrobenzene.*

*2-Iodo-4:6-dinitroaniline* is sparingly soluble in alcohol and more in toluene and crystallises from toluene in yellow crystals, m.p. 158°. (Found: N, 18.35.  $C_6H_4O_4N_3I$  requires N, 18.60 per cent).

*2-Iodo-4:6-dinitrodiphenylamine* dissolves easily in common organic solvents and crystallises from alcohol and acetic acid in orange crystals, m. p. 144°. (Found: N, 11.24.  $C_{12}H_8O_4N_3I$  requires N, 10.92 per cent).

*2-Iodo-4:6-dinitrodimethylaniline* easily dissolves in common organic solvents and crystallises from alcohol in orange-yellow silky needles, m. p. 112°. (Found: N, 12.16.  $C_8H_8O_4N_3I$  requires N, 12.47 per cent).

*Diiodotetranitrodiphenyl-p-phenylenediamine* is very sparingly soluble in alcohol and acetone and crystallises from acetic acid as

dark red crystals, m. p. above  $300^{\circ}$ . (Found: N, 12.48.  $C_{18}H_{10}O_8N_6I_2$  requires N, 12.15 per cent)

*2-Phenyl-7-iodo-5-nitropseudoaminobenzene* dissolves sparingly in alcohol and acetone and more easily in toluene and crystallises from it in shining colourless plates, m. p.  $192^{\circ}$ . (Found: N, 15.05.  $C_{18}H_7O_2N_4I$  requires N, 15.30 per cent) \*

*3:5-Dinitrophenoxazine* (m. p.  $214^{\circ}$ - $15^{\circ}$ ) is identical with the compound obtained from picryl chloride and 1-chloro-2-bromo-4:6-dinitrobenzene (*J. Chem. Soc.*, 1891, 59, 722; 1924, 125, 2481).

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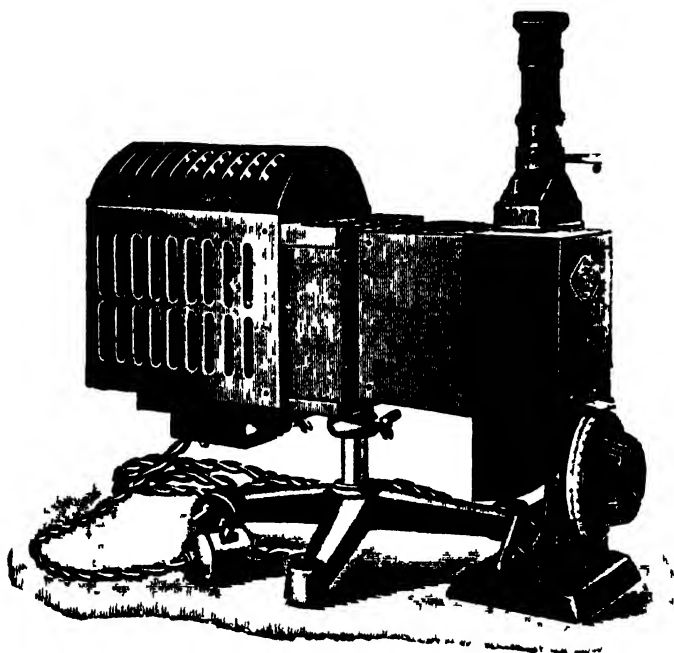
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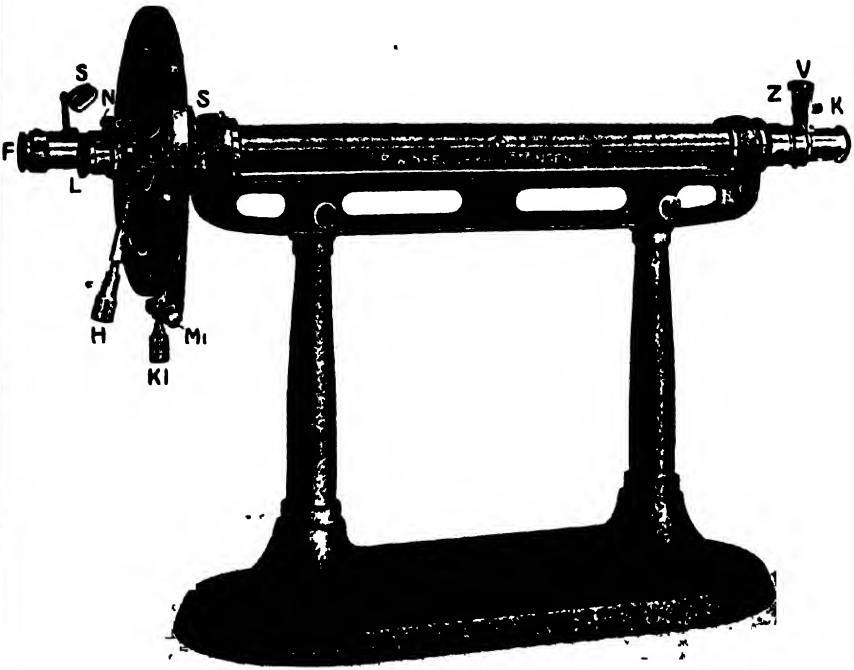
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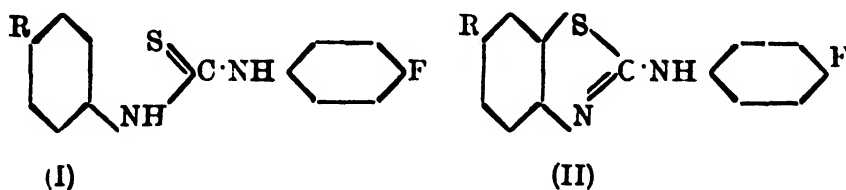
**BOMBAY**

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**The Directive Effect of Substituents on the Cyclisation  
of Substituted *s*-Diarylthiocarbamides. Part II.  
The Effect of the Fluorine Atom on the Thiazole  
Cyclisation of *p*-Fluoro-*s*-diphenylthio-  
carbamides by Bromine.**

BY MOHAMMAD OMAR FAROOQ AND ROBERT FERGUS HUNTER.

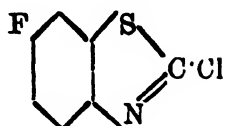
In view of the attention which has been directed in recent years by Ingold and his collaborators to the effect of fluorine substituents in aromatic substitution (Holmes and Ingold, *J. Chem. Soc.*, 1926, 1328; Ingold and Shaw, *ibid.*, 1927, 2918; Ingold and Vass, *ibid.*, 1928, 417; Ingold and Ingold, *ibid.*, p. 2254), it appeared of interest to include a study of the behaviour of *p*-fluoro-*s*-diphenylthiocarbamides (I) towards bromine in the present investigation (cf. Hunter, *J. Indian Chem. Soc.*, 1932, 9, 435).



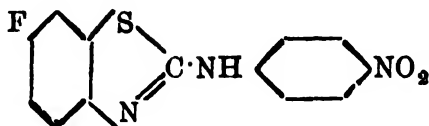
Under the usual conditions of thiazole cyclisation by bromine, the *p*-tolyl-, *p*-bromophenyl-, and 1-*p*-chlorophenylthiocarbamides (I, R=Me, Br and Cl respectively) gave rise to 4'-fluoro-1-anilinobenzthiazoles (II, R=Me, Br and Cl), identical with the bases obtained by condensation of *p*-fluoroaniline with the corresponding 5-substituted 1-chlorobenzthiazoles.

*s*-*p*-Fluorophenyl-*p* nitrophenylthiocarbamide (I, R=NO<sub>2</sub>), on the other hand, yielded a base isomeric with 4'-fluoro-5-nitro-1-anilino-benzthiazole (II, R=NO<sub>2</sub>) obtained from 5-nitrochlorobenzthiazole and *p*-fluoroaniline, which was shown to be 4'-nitro-5-fluoro-1-anilino-

benzthiazole (IV) by its synthesis from 5-fluoro-1-chlorobenzthiazole (III) and *p*-nitroaniline.



(III)



(IV)

The effect of the fluorine atom, therefore, falls into line with that of the other halogens previously studied (Dyson, Hunter and Soyka, *J. Chem. Soc.*, 1929, 458 ; Hunter and Jones, *J. Chem. Soc.*, 1930, 2190) ; the inhibitory effect of substituents on benzthiazole formation from thiocarbamilides being in the order  $\text{NO}_2 > \text{F} > \text{Cl} > \text{Br} > \text{EtO} > \text{Me}$  (cf. Hunter, Sir P. C. Ray Commemoration Volume, *J. Indian Chem. Soc.*, 1933, p. 79).

#### EXPERIMENTAL.

*s-p*-Fluorophenyl-*p*-tolylthiocarbamide (I, R=Me).—A solution of *p*-fluorophenylthiocarbamide (Dyson, Hunter, Jones and Styles, *J. Indian Chem. Soc.*, 1931, 8, 147) in ethyl acetate (2.3 g. in 8 c.c.) was mixed with a solution of *p*-toluidine (1.8 g) in the same solvent (8 c.c.) when a pale yellow colour developed and the mixture was concentrated on a steam-bath. On recrystallisation from ethyl acetate (charcoal), the *thiocarbamide* was obtained in glistening plates, m.p. 169°, yield 2.4 g. (Found: S, 12.7.  $\text{C}_{14}\text{H}_{13}\text{N}_2\text{FS}$  requires S, 12.3 per cent). In later experiments, the yield was raised to 2.7 g. by substituting benzene for ethyl acetate as the medium of condensation.

4-Fluoro-1-anilino-5-methylbenzthiazole (II, R=Me). (i) *Cyclisation of s-p-fluorophenyl-p-tolylthiocarbamide*.—Bromine (1.4 c.c. in 2 c.c. of chloroform) was added to a solution of the fluorphenyl-tolylthiocarbamide (0.8 g.) in chloroform (18 c.c.) and the mixture was heated on a steam-bath under reflux, when hydrogen bromide was copiously evolved during the first 10 minutes. Heating was continued for  $\frac{1}{2}$  hour and the resulting solution was concentrated under reduced pressure at laboratory temperature when the *hydropyrobromide* of the fluoroanilinobenzthiazole crystallised in yellow plates, which were collected on a porous earthenware and dried in vacuum. The bromo-addition compound was added to saturated sulphurous

acid and sulphur dioxide was passed through the mixture until the solid matter was colourless. On basification with ammonia (*d* 0.880) and recrystallisation from alcohol, 4'-fluoro-1-anilino-5-methylbenzthiazole was obtained in small crystals which had m. p. 182° alone, and when mixed with the specimen prepared from 1-chloro-5-methylbenzthiazole and *p*-fluoroaniline. (Found: S, 12.2.  $C_{14}H_{11}N_2FS$  requires S, 12.3 per cent).

(ii) *Synthesis from 1-chloro-5-methylbenzthiazole and p-fluoroaniline*.—A mixture of 1-chloro-5-methylbenzthiazole (0.9 g.) and *p*-fluoroaniline (0.6 g.) was heated in a wide mouth Pyrex boiling tube over a small naked flame for 2-3 minutes when a vigorous reaction took place. On basification with ammonia and recrystallisation from alcohol, 4'-fluoro-1-anilino-5-methylbenzthiazole was obtained in small crystals, m.p. 183°.

*s-p-Fluorophenyl-p-bromophenylthiocarbamide* (I, R=Br). prepared from *p*-fluorophenylthiocarbimide (3 g.) in benzene (10 c.c.) and *p*-bromoaniline (3.5 g.) in the same solvent (10 c.c.), separated from ethyl acetate in glistening plates, m.p. 159-60° (4.7 g.), which on further recrystallisation from benzene finally melted at 164-65°. (Found: S, 9.8.  $C_{13}H_{10}N_2BrFS$  requires S, 9.8 per cent).

4'-Fluoro-5-bromo-1-anilinobenzthiazole (II, R=Br). (i) *Cyclisation of s-p-fluorophenyl-p-bromophenylthiocarbamide*—The fluorophenylbromophenylthiocarbamide (0.5 g.) suspended in chloroform (10 c.c.), was treated with bromine (0.7 c.c. in 1 c.c. of chloroform) and the mixture was refluxed for 12 minutes and the *hydroperebromide* was collected on a porous earthenware and dried in a vacuum in the usual way. It formed orange yellow plates, m.p. 165-66°, which were added to sulphurous acid and treated with sulphur dioxide until all solid matter was colourless. On basification with ammonia and recrystallisation from alcohol, 0.45 g. of 4'-fluoro-5-bromo-1-anilinobenzthiazole, m.p. 210° was obtained. On repeated recrystallisation from ethyl acetate, in which the base is very soluble, the melting point was finally raised to 218-19°. A mixture of this with 4'-fluoro-5-bromo-1-anilinobenzthiazole obtained from the condensation of 1-chloro-5-bromobenzthiazole and *p*-fluoroaniline melted at 221-22°. In a similar experiment in which a suspension of the fluorophenylbromophenylthiocarbamide (0.8 g.) in chloroform (13 c.c.) was treated with bromine (1.5 c.c. in 1.5 c.c. of chloroform) and the mixture was heated under reflux for  $\frac{1}{2}$  hour, the first crop of 4'-fluoro-5-bromo-1-anilinobenzthiazole

obtained by recrystallisation of the base from the reduction of the hydroperbromide had m. p.  $216^{\circ}$ , and m. p.  $221-22^{\circ}$  when mixed with a genuine specimen. The second crop of crystals, however, had m. p.  $170^{\circ}$  which was further depressed by admixture with 4'-fluoro-5-bromo-1-anilinobenzthiazole and appeared to consist mainly of unchanged fluorophenylbromophenylthiocarbamide. A similar result was also obtained by treating a solution of fluorophenylbromophenylthiocarbamide (0.9 g.) in chloroform (25 c. c.) with bromine (1.6 c. c. in 2.5 c. c. of chloroform).

(ii) *Synthesis from 1-chloro-5-bromobenzthiazole and p-fluoro-aniline.*—An intimate mixture of 1-chloro-5-bromobenzthiazole (1.2 g.) and p-fluoroaniline (0.5 g.) was heated until a violent reaction took place. On basification with ammonia and recrystallisation from ethyl acetate, 4'-fluoro-5-bromo-1-anilinobenzthiazole was obtained in soft glistening plates, m. p.  $222-23^{\circ}$ . (Found: Br, 24.6; S, 10.1.  $C_{13}H_8N_2BrFS$  requires Br, 24.8; S, 9.9 per cent).

*s-p-Fluorophenyl-p-chlorophenylthiocarbamide*, prepared by condensation of benzene solutions of p-fluorophenylthiocarbimide (2.3 g.) and p-chloroaniline (1.9 g.), separated from benzene in glistening plates, m. p.  $158-59^{\circ}$ . (Found: S, 11.9.  $C_{13}H_{10}N_2ClFS$  requires S, 11.8 per cent).

*4'-Fluoro-5-chloro-1-anilinobenzthiazole.* (i) *Cyclisation of s-p-fluorophenyl-p-chlorophenylthiocarbamide.*—Bromine (1.6 c. c. in 2.5 c. c. of chloroform) was added to the fluorophenylchlorophenylthiocarbamide (0.9 g.) in chloroform (23 c. c.), and the mixture was heated under reflux for 30 minutes and cooled in ice. The bromo-addition compound was dried in vacuum in the usual way, suspended in sulphurous acid and treated with sulphur dioxide until reduction was complete. On basification and recrystallisation from alcohol—ethyl acetate, 4'-fluoro-5-chloro-1-anilinobenzthiazole was obtained which had m. p.  $218^{\circ}$ , and m. p.  $222^{\circ}$  when mixed with a specimen of the base obtained by condensation of 1:5-dichlorobenzthiazole with p-fluoroaniline. The base obtained from the mother liquors had m. p.  $172^{\circ}$  which rose to  $190^{\circ}$  when mixed with genuine 4'-fluoro-5-chloro-1-anilinobenzthiazole and contained thiocarbamide which had escaped cyclisation. In a similar experiment in which 0.7 g. of the fluorophenylchlorophenylthiocarbamide in chloroform (10 c. c.) was treated with bromine (1.4 c. c. in 2 c. c. of chloroform), 4'-fluoro-5-chloro-1-anilinobenzthiazole was isolated which had m. p.  $219-20^{\circ}$  alone, and m. p.  $220-22^{\circ}$  when mixed with a specimen obtained

from the dichlorobenzthiazole. In another experiment in which 0.5 g. of the thiocarbamide in chloroform (10 c.c.) was treated with bromine (0.8 c. c. in 1 c. c. of chloroform) and heating was continued for 43 minutes, the first crop of 4'-fluoro-5-chloro-1-anilinobenzthiazole obtained on recrystallisation from methyl alcohol had m. p. 218° alone, and m. p. 219-20° when mixed with a genuine specimen. The base obtained from the mother liquors, however, had m. p. 172° which rose to 184° on admixture with 4'-fluoro-5-chloro-1-anilinobenzthiazole, and contained free thiocarbamide which was detected by alkaline lead solution in the usual way.

(ii) *Synthesis from 1:5-dichlorobenzthiazole and p-fluoroaniline*.—An intimate mixture of 1:5-dichlorobenzthiazole (*vide* Part iii, p. 563) and *p*-fluoroaniline in equimolecular proportions was heated until a violent reaction took place. On basification and recrystallisation from alcohol—ethyl acetate, 4'-fluoro-5-chloro-1-anilinobenzthiazole was obtained in soft glistening plates, m. p. 222-23°. (Found: Cl, 12.7; S, 12.0.  $C_{13}H_8N_2ClFS$  requires Cl, 12.7; S, 11.9 per cent).

*s-p-Nitrophenyl-p-fluorophenylthiocarbamide*, prepared by condensation of equimolecular proportions of *p*-nitrophenylthiocarbimide (Dyson and George, *J. Chem. Soc.*, 1924, 125, 1702) and *p*-fluoroaniline in benzene, separated from absolute alcohol in pale yellow needles, m. p. 170-71°. (Found: S, 11.2.  $C_{13}H_{10}O_2N_3FS$  requires S, 11.1 per cent)

4'-Nitro-5-fluoro-1-anilinobenzthiazole (IV). (i) *Cyclisation of s-p-nitrophenyl-p-fluorophenylthiocarbamide*.—Bromine (1 c.c. in 1 c.c. of chloroform) was added to the nitrophenylfluorophenylthiocarbamide (0.5 g.) in chloroform (10 c.c.) and the mixture was heated under reflux for 30 minutes and kept overnight. The bromo-addition compound was collected, dried in vacuum and reduced with sulphurous acid in the usual way. On basification with ammonia (*d* 0.880) and recrystallisation from dilute alcohol, 4'-nitro-5-fluoro-1-anilinobenzthiazole was obtained in pale yellow crystals, m.p. 252-53°. (Found: S, 11.2.  $C_{13}H_8O_2N_3FS$  requires S, 11.1 per cent).

(ii) *Synthesis from 5-fluoro-1-aminobenzthiazole by way of 5-fluoro-1-chlorobenzthiazole*. (A). *5-Fluoro-1-chlorobenzthiazole*.—2 G. of 5-fluoro-1-aminobenzthiazole (Dyson, Hunter, Jones and Styles, *J. Indian Chem. Soc.*, 1931, 8, 147) in 10 c.c. of hydrochloric acid were diluted with water, cooled to 0° and diazotised with sodium nitrite (1 g. in 10 c.c. of water). A further 10 c.c. of concentrated hydrochloric acid were then added to the mixture which was boiled and

thereafter distilled in steam. The aqueous distillate was extracted with ether and the product obtained after removal of the ether on a steam-bath was recrystallised from methyl alcohol, when 5-fluorobenzthiazole was obtained in the form of soft silky needles, m.p. 97-98°, yield 0.45 g. (Found: Cl, 19.3.  $C_7H_3NClFS$  requires Cl, 19.0 per cent). (B). An intimate mixture of 5-fluoro-1-chlorobenzthiazole (0.1 g.) and *p*-fluoroaniline (0.08 g.) was heated in a test tube over a small flame until a violent reaction took place. On basification and recrystallisation from methyl alcohol—ethyl acetate, 4'-nitro-5-fluoro-1-anilinobenzthiazole was obtained which had m.p. 245° alone and m.p. 249-250° when mixed with the specimen obtained from *s-p*-nitrophenyl-*p*-fluorophenylthiocarbamide and bromine.

An attempt to prepare 5-fluoro-1-chlorobenzthiazole by heating *p*-fluorophenylthiocarbimide with phosphorus pentachloride in a sealed tube at 150-160° (*cf.* Hofmann, *Ber.* 1879, **12**, 1126; 1880, **13**, 8; Dyson, Hunter and Soyka, *J. Chem. Soc.*, 1929, 458) proved unsuccessful; the bulk of the fluorophenylthiocarbimide being recovered unchanged after 7 hours heating, accompanied by what appeared to be a derivative of phenylisocyanide dichloride.

*Synthesis of 4'-fluoro-5-nitro-1-anilinobenzthiazole from 5-nitro-1-chlorobenzthiazole and p-fluoroaniline.*—An intimate mixture of 1 g. of 5-nitro-1-chlorobenzthiazole (Part III, *loc cit.*) and *p*-fluoroaniline (0.55 g.) was condensed in the usual way and the basified product was recrystallised from ethyl acetate, when it was obtained in short pale greenish yellow crystals, m.p. 278-79°, yield 0.6 g. (Found: S, 11.3.  $C_{13}H_8O_2N_3FS$  requires S, 11.1 per cent). A mixture of this base with 4'-nitro-5-fluoro-1-anilinobenzthiazole (m.p. 252°) melted at 225°.



## Change of Stability of Sols of Various Concentrations with their Purity.

By S. GHOSH AND R. N. MITTRA.

Ghosh and Dhar (*J. Phys. Chem.*, 1927, **31**, 647) have shown that when a sol of uranium ferrocyanide is coagulated with a mixture of  $K_4Fe(CN)_6$  and KCl, the ionic antagonism is more marked in the case of the dilute sol than with a concentrated one.

It is evident from the coagulation experiments of Ghosh and Dhar (*loc. cit.*) on uranium ferrocyanide sol by KCl in the presence of  $K_4Fe(CN)_6$  that if the sol be mixed with some of  $K_4Fe(CN)_6$  which is a stabilising electrolyte, the sol would require more of KCl to coagulate a dilute sol than that necessary for a concentrated one, whilst the pure sol required the same amounts of KCl to coagulate the concentrated and dilute sols. In other words, if a sol contains an appreciable amount of stabilising electrolyte that gives the ion carrying the same charge as the colloid particle capable of being adsorbed by the colloid, the sol may behave abnormally on dilution towards its coagulation specially by univalent coagulating ions. This is easily explainable from the view developed by Ghosh and Dhar that the dilution effect and the behaviour towards a mixture of electrolytes are essentially connected and are mainly due to the same phenomenon of the adsorption of ions bearing the same charge as the colloid particles.

Recently Mittra and Dhar (*J. Indian Chem. Soc.*, 1932, **9**, 815) working with ferric hydroxide and aluminium hydroxide sols containing appreciable amounts of the stabilising electrolytes, found that these sols behave abnormally towards dilution. The same authors have noted that the sol of ferric hydroxide when freed from the stabilising substance, behaves normally towards dilution.

In this paper we have investigated the sol of thorium hydroxide by peptising thorium hydroxide precipitate with thorium nitrate and then subsequent dialysis. The following results have been obtained for the coagulation of the sols of different stages of purity at their various dilutions and also by a mixture of electrolytes.

*Thorium hydroxide sol.*

Purity\* = 1.26

Conc. of $\text{ThO}_2$ .	Amount of nitrate.	Ppt. conc. of $\text{KBrO}_3$ .
3.84 (g./litre)	0.863 (g./litre)	0.0531M
1.92	0.181	0.0562
0.96	0.090	0.0612

*Coagulation with mixture of  $\text{KBrO}_3$  and  $\text{K}_2\text{SO}_4$ .*Sol conc. = 3.84 g. of  $\text{ThO}_2$  per litre.

N/100- $\text{K}_2\text{SO}_4$ for complete coagulation.	N 8- $\text{KBrO}_3$ (c.c.)	...	0	4.25	0.5	1.0	2.0	4.0
	Obs. ..	2.1	0	1.85	1.65	1.25	0.25	
	Calc. ..	...	...	1.85	1.60	1.11	0.12	
	Diff. ..	...	...	...	0.05	0.14	0.13	

Purity = 12.2.

Conc. of $\text{ThO}_2$ .	Amount of nitrate.	Ppt. conc. of $\text{KBrO}_3$ .
3.84 (g./litre)	0.082 (g./litre)	0.024M
1.92	0.041	0.021
0.96	0.020	0.019

*Coagulation with mixture of  $\text{KBrO}_3$  and  $\text{K}_2\text{SO}_4$ .*Sol conc. = 3.84 g. of  $\text{ThO}_2$  per litre.

N/100- $\text{K}_2\text{SO}_4$ for complete coagulation.	N/8- $\text{KBrO}_3$ (c.c.)	Q	1.9	0.25	0.50	1.0	1.5
	Obs. ..	0.875	0	0.775	0.675	0.425	0.19
	Calc. ..	...	...	0.759	0.644	0.414	0.184
	Diff. ..	...	...	0.016	0.031	0.011	...

\* Purity is expressed as the ratio of the molar concentrations of the colloid and its stabilising substance.

It appears, therefore, from the foregoing results that if a sol is not sufficiently pure and contains large amounts of the stabilising electrolyte, the sol may behave abnormally towards its coagulation by univalent electrolytes on dilution, inspite of the fact that additive relationship is shown when the sol is coagulated by a mixture of electrolytes.

From a study of not less than twenty five sols,<sup>\*</sup> Ghosh and Dhar have come to the conclusion that when a sol is coagulated by an electrolyte, such that the ions carrying the same charge as the colloid particles are not adsorbed in appreciable amounts, (a) the sol behaves normally towards dilution, (b) shows additive relationship with mixture of electrolytes, and (c) does not develop the phenomenon of acclimatisation when coagulated by the addition of an electrolyte by parts. It is, therefore, obvious that the generalisations of Ghosh and Dhar on the coagulation of sols by electrolytes would be applicable in the case of pure sols. Moreover, in one of the publications from these laboratories Gore and Dhar (*J. Indian Chem. Soc.*, 1929, **6**, 641) pointed out that considerable change in physical properties of a sol is accompanied with the degree of purity of the sol. Desai (*Koll. Chem. Beih.*, 1928, **26**, 410 ; *Current Science*, 1932, **1**, 125) has shown that impure sols of some hydroxides behave abnormally on dilution towards their coagulation by KCl, LiCl, etc. When, however, the sols are purified by progressive dialysis the sols have a tendency to behave normally towards dilution when coagulated by the same univalent electrolytes. We are of opinion that this behaviour is due to the presence of sufficient quantities of stabilising electrolytes in the impure sols.

Recently Mukherjee and coworkers (*J. Indian Chem. Soc.*, 1930, **7**, 808) have investigated the stability of both positively and negatively charged manganese dioxide sols at various dilutions and report that their results are not in agreement with those obtained by Ghosh and Dhar (*J. Phys. Chem.*, 1927, **31**, 187). Mukherjee and coworkers find that both positively and negatively charged manganese dioxide sols require more of univalent coagulating ions to coagulate the diluted sols and at the same time additive relationships are obtained when the sols are coagulated by the mixture of ions of varying valencies.

Mukherjee and coworkers were unable to free their negatively charged manganese dioxide sol from impurities by dialysis. We have found that the proper cleaning of parchment paper for the dialysis of the sol with moderately concentrated  $\text{HNO}_3$  is necessary

in the preparation of the sol. The decomposition of  $\text{KMnO}_4$ , which is essentially the stabilising electrolyte, in unwashed parchment, is more and obviously renders the sol highly unstable. We have also noted that collodion bags are more suitable for dialysis than parchment bags. It is probably so, because collodion is less liable to decompose  $\text{KMnO}_4$  than the cellulose of the parchment paper. Using these bags we have again prepared a dialysed sol of manganese dioxide (negative) which has kept its stability for over a month. The sol used by Mukherjee and coworkers was not dialysed and hence it contained sufficient free  $\text{KMnO}_4$  and  $\text{KOH}$ .

Ghosh and Dhar prepared the positive sol of manganese dioxide by adding  $N/10\text{-FeCl}_3$  solution to a litre of the dialysed negative sol, whilst Mukherjee and coworkers obtained their positive sol by adding  $\text{H}_2\text{O}_2$  to a mixture of  $\text{FeCl}_3$  and  $\text{KMnO}_4$  solutions, and they have also analysed their sol. Their sol contains greater amounts of iron in comparison to the amount of manganese and they rightly conclude that their positively charged colloid of manganese dioxide may be either ferric manganate or complex solid containing different phases. We have analysed our dialysed positive sol of manganese dioxide with the following results:

Amount of total solid on evaporating 100 c.c. of the sol in a platinum crucible = 0.95 g.

Amount of Mn expressed as  $\text{MnO}_2$  per 100 c.c. of the sol = 0.88 g.

Amount of Fe expressed as  $\text{Fe}_2\text{O}_3$  per 100 c.c. of the sol = 0.05 g.

It is clear from the above that the amount of iron associated with manganese dioxide is considerably less and hence it is obvious that the sol obtained by Ghosh and Dhar is essentially different from that obtained by Mukherjee and coworkers. We have repeated the experiments on coagulation of dialysed sols of manganese dioxide both positive and negative, and have found that the results of Ghosh and Dhar are correct, and these sols behave normally towards dilution. We are of opinion that the results of Mukherjee and coworkers are different because of the method (*cf.* Mukherjee and Chaudhuri, *J. Chem. Soc.*, 1924, 125, 794) adopted by them for finding the precipitating concentrations of various electrolytes. It seems unsatisfactory to apply this method with the sols of various concentrations, which have certainly different degrees of transmission. With the coloured sols as those under investigation, it is obvious that the greater the concentration of the sol, the greater

the opacity. We have observed that these sols of  $\text{MnO}_2$  show partial coagulation and it is evident that a sol which is already of a higher opacity may become sufficiently opaque to make the filament of the lamp invisible with a quantity of electrolyte which may not be enough to cause complete coagulation.

We have carried out the following experiments on the coagulation of both positively and negatively charged manganese dioxide sols :

(a) To 8 c.c. of the positive sol 8 c.c. of  $N/200\text{-KCl}$  were added.

(b) 2 C.c. of the positive sol were made upto 8 c.c. with conductivity water and 8 c.c. of  $N/200\text{-KCl}$  were added. Both the concentrated and dilute sols were kept for 10 minutes.

(c) After 10 minutes have elapsed 4 c.c. of the mixture of the concentrated sol and the electrolyte, were added to 12 c.c. of  $N/400\text{-KCl}$ , thus keeping the concentration of the electrolyte the same as present in the concentrated and dilute sols in (a) and (b). After 2 minutes (b) and (c) were taken in a double absorption cell and it was found with a Nutting's photometer that the extinction coefficient of (c) was less by 0.04 than that of (b). This experiment conclusively proves that the stage of coalescence is definitely greater with a diluted positive sol of manganese dioxide than with a concentrated one. Similar results were obtained with the negative sol of manganese dioxide of various dilutions.

Hence we are of opinion that the positively and negatively charged sols of manganese dioxide behave normally towards dilution when coagulated by such electrolytes as  $\text{KCl}$ ,  $\text{KNO}_3$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{BaCl}_2$ , etc., and prove that the previous results of Ghosh and Dhar are correct.

#### CONCLUSION.

From a study of not less than twenty five sols Ghosh and Dhar have concluded that when the sol is coagulated with an electrolyte such that the ions carrying the same charge as the colloid particles is not adsorbed in appreciable amounts, (a) the sol behaves normally towards dilution when coagulated by ions of varying valencies, (b) does not develop ionic antagonism, and (c) does not show the phenomenon of acclimatisation. From the experimental results it is shown that if a sol is not sufficiently pure and contains large amounts of the stabilising electrolyte, the sol may behave abnormally towards

the coagulation by univalent electrolytes on dilution inspite of the fact that additive relationship is shown when the sol is coagulated by a mixture of electrolytes.

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## Limitations of Solubility Method for Determining Dissociation Constant.

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The solubility of sparingly soluble acid is increased in a solution of sodium salt of a weak acid is well known, and the quantitative measurements of the actual increase have been made by Noyes and Chappin (*Z. physikal. Chem.*, 1898, 27, 442), Philip (*J. Chem. Soc.*, 1905, 87, 987), Philip and Garner (*ibid.*, 1903, 95, 1466) and by Bhagwat and Dhar (*J. Indian Chem. Soc.*, 1929, 6, 807).

Noyes (*Z. physikal. Chem.*, 1898, 27, 273) has deduced an equation from which the solubility of a sparingly soluble acid in the sodium salts of weak acids can be calculated. Dhar (*J. Amer. Chem. Soc.* 1913, 35, 800) has deduced a formula for finding out the dissociation constant of weak acids. He has shown that if 'a', be the solubility of the weak acid in water,  $K_1$ , its dissociation constant, 'b', the solubility of the acid in the concentration 'c', of the sodium salt of the weak acid whose dissociation constant  $K_2$  is required then,

$$K_2 = \frac{K_1 \times a (c - b + a)}{(b - a)^2} \quad \dots (1)$$

Dhar and Dutta (*Z. Elektrochem.*, 1913, 19, 407) have shown that this formula is applicable for very low concentrations of sodium salts. They have employed the solubility results of Philip (*loc. cit.*), and Philip and Garner (*loc. cit.*) for this purpose. All the acids considered by them were monobasic. This work was extended to dibasic acid as carbonic acid with whose help the dissociation constant of the acid of the sodium salt was determined. Datta and Dhar (*J. Chem. Soc.*, 1915, 107, 824) observed that the above equation has to be modified and they showed

$$K_2 = \frac{K_1 \times a [c - 2(b - a)]}{(b - a)^2} \quad \dots (2)$$

The applicability of the equation (1) has been verified also by Bhagwat and Dhar (*J. Indian Chem. Soc.*, 1929, 6, 806) in case of numerous acids and they have shown that equation (2) is incorrect and the general formula for finding the dissociation constant when

the basicity of sparingly soluble acid is  $n$ , has been deduced, taking into consideration the degrees of ionisation of salts and acids in solution. Thus,

$$K_2 = \frac{nK_1 (1 - K_3) \times a [nK_2c - K_4 (b - a)]}{K_3 \times K_4 (b - a)^2} \dots (3)$$

If we introduce the conception that the salts are completely ionised and acids do not ionise at all then,

$$K_2 = \frac{nK_1 \times a [nc - (b - a)]}{(b - a)^2} \dots \dots (4)$$

In this paper we have fully considered the limit of the concentration of sodium salt up to which these formulae hold and explanation has been forwarded for the deviations observed. For this purpose we have varied the concentrations of sodium salts over a very wide range and the results are recorded in the following tables.

#### A. Dissociation Constant of Formic Acid.

With benzoic acid at  $30^\circ$ . Dissociation constant  $K_1$  of benzoic acid  $= 6.4 \times 10^{-5}$  at  $30^\circ$ .  $a = 0.03306$ .

$a$ .	$b$ .	$b - a$ .	$c - b + a$ .	$K_2 = \frac{K_1 a (c - b + a)}{(b - a)^2}$ .
0.0596	0.05196	0.01890	0.04072	$2.3 \times 10^{-4}$
0.0855	0.05708	0.02402	0.06548	2.3
0.1790	0.06889	0.03583	0.1431	2.26
0.3158	0.08064	0.04758	0.2682	2.4
0.4211	0.08951	0.05645	0.3646	2.3
0.6816	0.1008	0.056774	0.5639	2.49
1.2355	0.1340	0.1009	1.1346	2.26
1.6474	0.1466	0.1135	1.5338	2.4
2.4711	0.1666	0.1335	2.3375	2.6

It will be seen from these results that the value of dissociation constant is more or less constant over a wide range (from 0.0596  $N$  to 2.4711  $N$  or from 4.0541 g. to 168.0356 g. per litre), although there is a tendency to increase for the value of the dissociation constant when concentration of the sodium salt increases.



With salicylic acid at 80°.  $K_1$  of salicylic acid =  $1.6 \times 10^{-3}$  at 25°.  $a = 0.01987$ .

$c$ .	$b$ .	$b-a$ .	$c-b+a$ .	$K_2 = \frac{K_1 a (c-b+a)}{(b-a)^2}$ .
0.06832	0.06248	0.04261	0.02571	$2.81 \times 10^{-4}$
0.1008	0.07501	0.05514	0.4567	2.98
0.1823	0.0875	0.06763	0.6468	2.8
0.1924	0.1097	0.08983	0.1026	2.52
0.3528	0.1525	0.1326	0.2202	2.48
0.4887	0.1913	0.1714	0.3173	2.1
0.5292	0.1961	0.1762	0.3530	2.25
0.7056	0.2325	0.2126	0.5930	2.61
1.0585	0.2925	0.2726	0.7858	2.1
2.1170	0.4614	0.4415	1.6755	1.7

It will be seen from the above results that the value of dissociation constant is more or less constant over a wide range (from 0.06832N to 2.1170N or from 4.6456 g. to 144.0145 g. per litre), although there is a tendency to decrease the value of dissociation constant as the concentration of the sodium salt increases.

#### B. Dissociation Constant of Acetic Acid.

With benzoic acid at 30°.  $K_1$  of benzoic acid at 30° =  $6.4 \times 10^{-5}$ .  $a = 0.03306$ .

$c$ .	$b$ .	$b-a$ .	$c-b+a$ .	$K_2 = \frac{K_1 a (c-b+a)}{(b-a)^2}$ .
0.03232	0.06107	0.0280	0.00482	$1.25 \times 10^{-5}$
0.06565	0.08196	0.0489	0.01675	1.42
0.08128	0.0909	0.05784	0.02344	1.42
0.1067	0.1010	0.06794	0.03874	1.7
0.1739	0.1326	0.09951	0.07446	1.5
0.2008	0.1452	0.11214	0.08867	1.46
0.2475	0.1603	0.1272	0.1230	1.53
0.3413	0.1896	0.1565	0.1848	1.52
0.4267	0.2121	0.1790	0.2477	1.57
0.4950	0.2260	0.1930	0.3090	1.64
0.7425	0.2755	0.2425	0.5000	1.72
0.9900	0.3145	0.2815	0.7085	1.81
1.4850	0.3949	0.3618	1.1232	1.74

It will be seen from the above results that the value of dissociation constant is more or less constant over a wide range (from 0.03282N to 1.4850N or from 2.2822 g. to 201.9644 g. per litre), although there is a tendency to increase the value of the dissociation constant as the concentration of the sodium salt increases.

With *salicylic acid* at 30°. Dissociation constant  $K_1$  of *salicylic acid* =  $1.0 \times 10^{-3}$  at 25°.  $a = 0.01987$ .

c.	b.	b-a.	c-b+a.	$K_1 = \frac{K_1 a(c-b+a)}{(b-a)^2}$
0.01731	0.03499	0.01512	0.00219	$1.9 \times 10^{-4}$
0.02597	0.04375	0.02388	0.00109	$7.2 \times 10^{-5}$
0.05194	0.08625	0.04638	0.00556	5.1
0.07666	0.0850	0.06513	0.01154	5.4
0.14636	0.1400	0.1201	0.02623	2.87
0.2683	0.2250	0.2151	0.05321	2.99
0.3220	0.2625	0.2426	0.07937	2.68
0.5366	0.4150	0.3951	0.1415	1.81
0.8050	0.5611	0.5412	0.2339	1.78
1.610	1.0380	1.0481	0.5618	1.02

It will be seen from the above results that the value of dissociation constant is practically of the same order between the range investigated (from 0.01731N to 1.61N or from 2.3547 g. to 218.9932 g. per litre) and gradually decreases as the concentration of the sodium salt is increased.

With *cinnamic acid* at 30°. Dissociation constant  $K_1$  of *cinnamic acid* at 25° =  $8.51 \times 10^{-5}$ .  $a = 0.004688$ .

c.	b.	b-a.	c-b+a.	$K_1 = \frac{K_1 a(c-b+a)}{(b-a)^2}$
0.01731	0.01111	0.00722	0.01009	$3.18 \times 10^{-5}$
0.02597	0.01577	0.01108	0.01488	1.99
0.05194	0.01964	0.01495	0.03698	2.72
0.07666	0.02381	0.01912	0.05754	2.59
0.1463	0.03274	0.02805	0.1183	2.46
0.2634	0.04485	0.03966	0.2286	2.44
0.3220	0.04881	0.04412	0.2378	2.34
0.5366	0.06190	0.05721	0.4794	2.41
0.8050	0.07501	0.07082	0.7846	2.39
1.6100	0.1244	0.1197	1.5908	1.82

It will be seen from the above results that the value of dissociation constant is more or less constant over a wide range (from 0.01781N to 1.61N or from 2.8574 g. to 218.9932 g. per litre), although there is a tendency to decrease the value of dissociation constant as the concentration of the sodium salt increases.

### C. Dissociation Constant of Cirtic Acid.

With benzoic acid at 30°. Dissociation constant  $K_1$  of benzoic acid =  $6.4 \times 10^{-5}$  at 30°.  $a = 0.03306$ .

c.	b.	b-a.	c-b+a.	$K_1 = \frac{a(c-b+a)}{(b-a)^2}$
0.04512	0.06152	0.02846	0.01668	$4.3 \times 10^{-5}$
0.06666	0.07308	0.04202	0.02664	4.2
0.12717	0.10260	0.06954	0.05763	2.5
0.23313	0.14170	0.10864	0.1245	2.27
0.27978	0.1577	0.12464	0.1531	1.78
0.4662	0.2051	0.1720	0.2942	1.67
0.6996	0.2475	0.2144	0.4852	2.23
0.9324	0.2793	0.2462	0.6862	2.45
1.3989	0.3205	0.2874	1.1117	2.85

It will be seen from the above results that the value of dissociation constant is more or less constant over a wide range (from 0.04512N to 1.3989N or from 5.3701 g. to 166.4754 g. per litre), although the value of dissociation constant first decreases and then increases with the increase of the concentration of the salt.

With salicylic acid at 80°. Dissociation constant  $K_1$  of salicylic acid =  $1.0 \times 10^{-3}$  at 25°.  $a = 0.01987$ .

c.	b.	b-a.	c-b+a.	$K_1 = \frac{a(c-b+a)}{(b-a)^2}$
0.04512	0.05706	0.03719	0.00793	$1.14 \times 10^{-4}$
0.06666	0.07435	0.05448	0.1218	$8.19 \times 10^{-5}$
0.12717	0.1153	0.03543	0.3174	6.93
0.23313	0.1807	0.1608	0.07233	5.56
0.27978	0.2154	0.1955	0.08428	4.86
0.4662	0.3128	0.2999	0.1733	4.01
0.6996	0.4141	0.3943	0.3054	3.90
0.9324	0.5211	0.5013	0.4312	3.41
1.3989	0.6577	0.6378	0.7611	3.73

It will be clear from the above results that the value of dissociation constant is practically of the same order, between the range examined (from 0.04512N to 1.3989N or from 5.3701 g. to 166.4754 g. per litre). Clearly there is a tendency to decrease the dissociation constant as the concentration of the sodium salt increases.

With *cinnamic acid* at 30°. Dissociation constant  $K_1$  of cinnamic acid =  $3.51 \times 10^{-5}$  at 25°.  $a = 0.0046875$ .

$c$ .	$b$ .	$b - a$ .	$c - b + a$ .	$K_2 = \frac{K_1 a (c - b + a)}{(b - a)^2}$ .
0.04512	0.02344	0.01875	0.02637	$1.23 \times 10^{-4}$
0.06666	0.02917	0.02448	0.04218	1.16
0.12717	0.04271	0.03802	0.08915	1.01
0.23313	0.05729	0.05260	0.1805	1.1
0.27978	0.06353	0.05884	0.2209	1.05
0.4662	0.07812	0.07343	0.3927	1.2
0.6996	0.08646	0.08177	0.6178	1.5
0.9324	0.09246	0.08777	0.8446	1.8
1.3989	0.09790	0.09332	1.3057	2.5

It will be clear from the above results that the value of dissociation constant is more or less constant over a wide range (from 0.04512N to 1.3982N or from 5.3701 g. to 166.4754 g. per litre), although there is a tendency to increase the dissociation constant as the concentration of the salt increases.

#### D. Dissociation Constant of Benzoic Acid.

With *cinnamic acid* at 16.3°. Dissociation constant  $K_1$  of cinnamic acid =  $3.51 \times 10^{-5}$  at 25°.  $a = 0.002643$ .

$c$ .	$b$ .	$b - a$ .	$c - b + a$ .	$K_2 = \frac{K_1 a (c - b + a)}{(b - a)^2}$ .
0.01201	0.005288	0.002645	0.009365	$1.24 \times 10^{-4}$
0.02403	0.006901	0.004258	0.01977	$1.01 \times 10^{-4}$
0.04806	0.009410	0.006767	0.04128	$8.86 \times 10^{-5}$
0.1201	0.01399	0.01135	0.1087	7.68
0.24028	0.02025	0.01761	0.2227	6.66
0.4004	0.02845	0.02581	0.3747	5.92
0.6007	0.03459	0.03195	0.5687	5.17
0.9009	0.03769	0.03499	0.7659	5.81

It will be clear from the above results that the value of dissociation constant steadily decreases with the increase of the concentration. The concentration of sodium benzoate ranges from 0.01201N to 0.8009N or from 1.7806 g. to 115.3787 g. per litre.

With salicylic acid at 14.5°. Dissociation constant  $K_1$  of salicylic acid =  $9.5 \times 10^{-4}$  at 20°.  $a = 0.01209$ .

c.	b.	b-a.	c-b+a.	$K_2 = \frac{K_1 a(c-b+a)}{(b-a)^2}$
0.01201	0.01758	0.00549	0.00652	$2.48 \times 10^{-3}$
0.02402	0.02459	0.01250	0.01152	8.47
0.04804	0.02774	0.01565	0.03239	1.52
0.1201	0.03022	0.01813	0.01020	3.56
0.2402	0.08035	0.01826	0.02219	7.64
0.4003	0.03215	0.02006	0.3802	$1.09 \times 10^{-3}$
0.6005	0.03105	0.01896	0.5815	1.86
0.8006	0.03270	0.02061	0.7799	2.11
1.201	0.03956	0.02747	1.1735	2.58

It will be clear from the above results that the value of dissociation constant gradually increases with the increase of the concentration. The concentration of the sodium benzoate ranges from 0.01201N to 1.201N or from 1.7306 g. to 173.0606 g. per litre.

#### E. Dissociation Constant of Salicylic Acid.

With benzoic acid at 30°. Dissociation constant of  $K_1$  of benzoic acid =  $6.2 \times 10^{-5}$  at 30°.  $a = 0.03306$ .

c.	b.	b-a.	c-b+a.	$K_2 = \frac{K_1 a(c-b+a)}{(b-a)^2}$
0.05899	0.03339	0.00033	0.05866	$1.14 \times 10^{-1}$
0.08693	0.03485	0.00179	0.08514	$5.6 \times 10^{-3}$
0.1659	0.00124	0.00818	0.1578	$4.99 \times 10^{-3}$
0.3043	0.04742	0.01436	0.2899	$2.97 \times 10^{-3}$
0.3651	0.06438	0.02132	0.3438	$1.6 \times 10^{-3}$
0.4564	0.06912	0.02606	0.4303	$1.34 \times 10^{-3}$
0.6065	0.06333	0.06027	0.5582	$4.67 \times 10^{-4}$
0.9128	0.1125	0.07947	0.8334	$2.79 \times 10^{-4}$
1.217	0.1805	0.1475	1.0695	$1.04 \times 10^{-4}$
1.8255	0.2764	0.2433	1.5822	$5.66 \times 10^{-5}$

It will be clear from the above results that the formula does not give constant value for  $K_2$ . The values of dissociation constant decrease with the increase of concentration of the sodium salicylate. The concentration of sodium salicylate ranges from 0.05889N to 1.8255N or from 9.4220 g. to 292.08 g. per litre.

With succinic acid at 84.8°. Dissociation constant  $K_1$  of succinic acid =  $6.6 \times 10^{-5}$  at 25°.  $a = 0.8515$ .

c.	b.	b - a.	c - b + a.	$K_2 = \frac{K_1 a(c - b + a)}{(b - a)^2}$
0.07238	1.0000	0.1485	Negative	...
0.1882	1.0820	0.2805	"	...
0.2583	1.2030	0.3515	"	...
0.5066	1.4060	0.5545	"	...
0.7600	1.5880	0.7365	"	...
1.0133	1.6580	0.8065	0.0235	$2.43 \times 10^{-4}$
1.5200	1.4710	0.6195	0.2068	$1.79 \times 10^{-4}$
			0.9005	$1.32 \times 10^{-4}$

It will be seen from the above results that the values of  $c - b + a$  are negative or the formula for determining dissociation constant breaks down completely in this case, although at very high concentration we get positive results. The concentration of the salt ranges from 0.07238N to 1.52N or from 11.58 g. to 243.2 g. per litre.

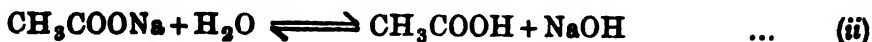
#### DISCUSSION.

All the workers mentioned above have not taken into consideration the hydrolysis of these salts of weak acid and in this discussion we have fully studied the various types of equilibria which can exist and the various relations obtained from their considerations.

Let us consider an acid, say,  $C_6H_5COOH$  which is a weak acid and its solubility in water 'a'. Let us also consider the sodium salt of another weak acid, say, acetic acid and let the solubility of benzoic acid in the concentration 'c', of the sodium acetate 'b'. Then under equilibrium we have,



The salts  $\text{CH}_3\text{COONa}$  and  $\text{C}_6\text{H}_5\text{COONa}$  being those of weak acid partly hydrolyse, thus



Hence the hydrolytic constant  $K_7$  of  $\text{CH}_3\text{COONa}$  is given by

$$K_7 = \frac{[\text{CH}_3\text{COOH}][\text{NaOH}]}{[\text{CH}_3\text{COONa}][\text{H}_2\text{O}]} \quad \dots \quad \dots \quad \dots \quad (\text{iv})$$

where  $[\text{CH}_3\text{COOH}]$ ,  $[\text{NaOH}]$ ,  $[\text{CH}_3\text{COONa}]$ , etc., represent the concentrations of  $\text{CH}_3\text{COOH}$ ,  $\text{NaOH}$ ,  $\text{CH}_3\text{COONa}$  etc., in equilibrium.

The equilibrium concentration of water being constant we can write

$$K_8 = \frac{[\text{CH}_3\text{COOH}][\text{NaOH}]}{[\text{CH}_3\text{COONa}]} \quad \dots \quad \dots \quad \dots \quad (\text{v})$$

where  $K_8 = K_7 [\text{H}_2\text{O}]$ . Similarly, if  $K_9$  is the hydrolytic constant of  $\text{C}_6\text{H}_5\text{COONa}$

$$K_9 = \frac{[\text{C}_6\text{H}_5\text{COOH}][\text{NaOH}]}{[\text{C}_6\text{H}_5\text{COONa}]} \quad \dots \quad \dots \quad \dots \quad (\text{vi})$$

where  $[\text{C}_6\text{H}_5\text{COOH}]$ ,  $[\text{NaOH}]$ , etc., represent the concentrations of  $\text{C}_6\text{H}_5\text{COOH}$ ,  $\text{NaOH}$ , etc

But the equation (i) being in equilibrium with the equations (ii) and (iii) they must be simultaneously satisfied.

$$\text{From (v) we have } [\text{NaOH}] = \frac{K_8 [\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]} \quad \dots \quad (\text{vii})$$

$$\text{From (vi) we have } [\text{NaOH}] = \frac{K_9 [\text{C}_6\text{H}_5\text{COONa}]}{[\text{C}_6\text{H}_5\text{COOH}]} \quad \dots \quad (\text{viii})$$

$$\text{Hence, } \frac{K_8 [\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]} = \frac{K_9 [\text{C}_6\text{H}_5\text{COONa}]}{[\text{C}_6\text{H}_5\text{COOH}]}$$

$$\text{or, } \frac{K_8}{K_9} = K = \frac{[\text{C}_6\text{H}_5\text{COONa}][\text{CH}_3\text{COOH}]}{[\text{C}_6\text{H}_5\text{COOH}][\text{CH}_3\text{COONa}]} \quad \dots \quad (\text{ix})$$

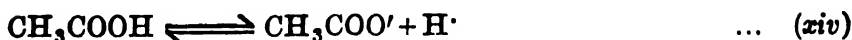
From the equation (i) it is clear that in equilibrium the concentrations of  $C_6H_5COOH$ ,  $CH_3COONa$ ,  $CH_3COOH$  and  $C_6H_5COONa$  are respectively  $a$ ,  $c-b+a$ ,  $b-a$ , and  $b-a$ .

$$\text{Hence, } K = \frac{K_8}{K_9} = \frac{(c-b+a) \times a}{(b-a)} \quad \dots (x)$$

Moreover,  $NaOH$  ionises completely. Therefore the concentration of  $[OH]$  is given by

$$[OH] = \frac{K_8(c-b+a)}{(b-a)} \quad \dots (xi)$$

$$= \frac{K_9(b-a)}{a} \quad \dots (xii)$$



$$\text{Hence, } \frac{[C_6H_5COO][H]}{[C_6H_5COOH]} = K_{10} \quad \dots (xv)$$

$$\text{and } \frac{[CH_3COO][H]}{[CH_3COOH]} = K_{11} \quad \dots (xvi)$$

where  $K_{10}$  and  $K_{11}$  are the dissociation constants of the acids. But according to the equation (i) the equations (xv) and (xvi) must be simultaneously satisfied. Hence,

$$\frac{K_{11}}{K_{10}} = \frac{[CH_3COO][C_6H_5COOH]}{[CH_3COOH][C_6H_5COO]}.$$

Assuming that salts ionise completely and the weak acids do not ionise at all we get

$$\frac{K_{11}}{K_{10}} = \frac{(c-b+a) \times a}{(b-a)^2} \quad \dots (xvii)$$

$$\text{Moreover, } [H] = \frac{K_{10}[C_6H_5COOH]}{[C_6H_5COO]} = \frac{K_{11}[CH_3COOH]}{[CH_3COO]}$$



$$[H] = \frac{K_{10} \times a}{b-a} = \frac{K_{11}(b-a)}{c-b+a} \quad \dots \quad (xviii)$$

Also water ionises as  $H_2O \rightleftharpoons H + OH$  ... (xix)

or  $[H] \cdot [OH] = K_w$  ... (xx)

where  $K_w$  is the ionisation constant of water. From equations (xviii) and (xii) we have

$$\frac{K_{10} \times a}{b-a} \times \frac{K_9(b-a)}{a} = K_w \quad \text{or} \quad K_{10}K_9 = K_w \quad \dots \quad (xxi)$$

and  $K_{11}K_8 = K_w$  ... (xxii) [from equations (xviii) and (xi)].

Hence,  $\frac{K_{10}}{K_8} = \frac{K_{11}}{K_9}$  ... (xxiii) or,  $\frac{K_{10}}{K_{11}} = \frac{K_8}{K_9}$

which also follows from the equations (xvii) and (x). These equations show that the formulae for determining dissociation constant show maximum accuracy when the dissociation constants of the acid investigated and of the acid employed are identical or more or less of the same order. It will be seen from the results that the conclusion is borne out by the experiments

Our results of the dissociation constant show that with benzoic acid the values of dissociation constant obtained, increases in case of formic and acetic acid as the concentration of sodium salt is increased. Similar is the case for the values of dissociation constant of benzoic acid with salicylic acid, and citric acid with cinnamic acid. This may be explained from the view point that  $(b-a)$ , the rate of increase in solubility diminishes with the concentration of sodium salt, for with the increase in concentration of sodium salt the degree of hydrolysis of these salts diminishes and hence the amount of acid dissolved to balance this decrease.

However, the values of the dissociation constant with benzoic acid for salicylic acid goes on increasing with the dilution of the sodium salt. Same thing is observed for formic acid, acetic acid and citric acid with salicylic acid and for acetic acid and salicylic acid with cinnamic acid. In deducing the equation

$$K_2 = \frac{K_1 \times a(c-b+a)}{(b-a)^2}$$

it has been shown that  $(b-a)$  also represents the amount of undissociated acid. In this simple formula we have neglected the ionisation of the acid which increases with the dilution or the amount of undissociated molecules decreases. Therefore  $(b-a)$  decreases with dilution and  $(c-b+a)$  increases with dilution. It is therefore quite clear that  $K_2$  should increase with dilution.

Thus it appears that there are two factors in these cases, the hydrolysis and ionisation and they act in reverse way. With the increase in concentration degree of hydrolysis decreases and therefore  $(b-a)$ , the increase in solubility diminishes while the degree of ionisation diminishes and hence the number of undissociated molecules or  $(b-a)$  increases. Hence, according as one factor predominates over the other, the dissociation constant increases or decreases with the concentration of the sodium salt.

This conclusion seems to be supported by our observation of the values of dissociation constants of citric acid with benzoic acid.

It is more or less generally observed that weaker the acid, lower is the dissociation constant obtained. It has been shown by Bhagwat and Dhar (*loc. cit.*) that the cause of low dissociation constant for weaker acid is the greater hydrolysis of its sodium salt.

Our results for the dissociation constant of salicylic acid with succinic acid are negative at low concentration of the sodium salt when the simple formula is employed. But the succinic acid is dibasic and hence Bhagwat and Dhar's general formula should be applied. It is noteworthy to find that this formula gives positive results.

$K_1$  for succinic acid  $= 6.6 \times 10^{-5}$  at  $25^\circ$ .  $a = 0.8515$ .

$2c.$	$b.$	$b-a.$	$(2c-b-a).$	$K_2 = \frac{2K_1 a (2c-b+a)}{(b-a)^2}$
0.2764	1.0820	0.2305	0.0459	$6.11 \times 10^{-5}$
0.5066	1.2030	0.3515	0.1551	7.05
1.0132	1.4060	0.5545	0.4487	8.19
1.5200	1.5280	0.7865	0.7835	1.08
2.0266	1.6580	0.8065	1.2001	$1.04 \times 10^{-4}$
3.3400	1.4710	0.6195	2.7205	$8.98 \times 10^{-4}$

Although we cannot speak of the dissociation constant of hydrochloric acid, yet it is interesting to observe that the formula which is

derived only for weak acids is well applicable even for such a strong acid as hydrochloric acid and gives a constant value for  $K_2$  which may be called the solubility constant for hydrochloric acid and with its help the solubility of an acid at any other concentration of the sodium chloride can be determined.

The following table gives the limit of applicability of solubility method for finding out the dissociation constant.

Acid used for finding $K_2$ .	Na salt used.	Range of Na salt investigated.	Value obtained for $K_2$ at 30°.	Real value for $K_2$ at 25°.	Limit of applicability
Benzoic	Sodium formate	0.0N-2.4711N	$2.4 \times 10^{-4}$	$2.1 \times 10^{-4}$	All
Salicylic	„	0.0N-2.117N	$2.4 \times 10^{-4}$	$2.1 \times 10^{-4}$	All; strictly for intermediate conc.
Benzoic	Sodium acetate	0.0N-1.485N	$1.6 \times 10^{-5}$	$1.8 \times 10^{-5}$	All; strictly for high conc.
Salicylic	„	0.0N-1.610N	$1.8 \times 10^{-5}$	$1.8 \times 10^{-5}$	At high conc. only
Cinnamic	„	0.0N-1.610N	$2.4 \times 10^{-5}$	$1.8 \times 10^{-5}$	At high conc. only
Benzoic	Sodium citrate	0.0N-1.3989N	$2.2 \times 10^{-5}$	$8 \times 10^{-4}$	Not applicable
Salicylic	„	0.0N-1.3989N	$5.5 \times 10^{-5}$	$8 \times 10^{-4}$	Do
Cinnamic	„	0.0N-1.3989N	$1.8 \times 10^{-4}$	$8 \times 10^{-4}$	Do
Cinnamic	Sodium benzoate	0.0N-0.800N	$6.65 \times 10^{-4}$	$6.4 \times 10^{-4}$	Applicable for intermediate conc.
Salicylic		0.0N-0.240N	$1.09 \times 10^{-3}$	$6.4 \times 10^{-3}$	Not applicable
Benzoic	Sodium salicylate	0.0N-1.825N	$1.0 \times 10^{-3}$	$1.0 \times 10^{-3}$	Applicable for intermediate conc.

It is thus clear that the formula is strictly true when  $K_1$  and  $K_2$  are very nearly of the same magnitude, as shown by theoretical considerations.

## SUMMARY.

1. Dissociation constant of formic acid, acetic acid, salicylic acid and citric acid, has been determined by the formula

$$K_2 = \frac{K_1 - a(c - b + a)}{(b - a)^2}$$

and the limit of concentration for which this equation holds has been thoroughly discussed.

2. It is shown that in some cases dissociation constant of the acid diminishes with the lowering of the concentration of its sodium salt and in some cases it increases with the dilution. It has been shown that two factors are acting in reverse way, hydrolysis of the salt and the degree of ionisation. With dilution degree of ionisation and hydrolysis increases but the former diminishes the number of acid molecules or  $(b - a)$ , while the latter increases the solubility,  $(b - a)$ . Thus when the former is increasing the value of dissociation constant the latter causes it to diminish and the observed result is due to one which is predominating.

3. The value of dissociation constant is greater when stronger acid is used for determining the value. This is explained on the basis of hydrolysis.

4. Various equilibria in solution of weak acid in solution of salt of weak acid have been discussed and their relationship studied. It is shown from these equations that the formula is applicable strictly when the dissociation constants of the acid investigated and employed are identical.

5. The above formula for finding the dissociation constant gives negative results with succinic acid. It is shown that Bhagwat and Dhar's general formula is applicable

$$K_n = \frac{nK - a(nc - b + a)}{(b - a)^2}$$

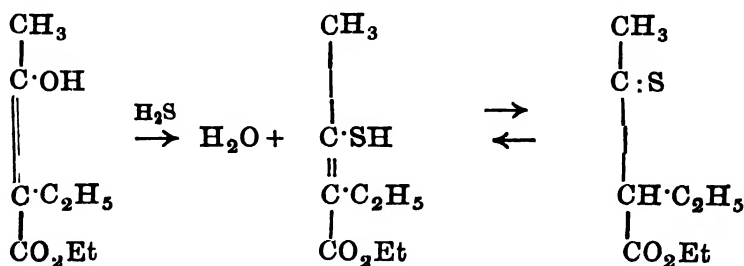
where  $n$  is the basicity of the acid employed, it being 2 in this case.

6. Although the formula is derived only for weak acids it is found to obey to some extent even for such a strong acid as hydrochloric acid.

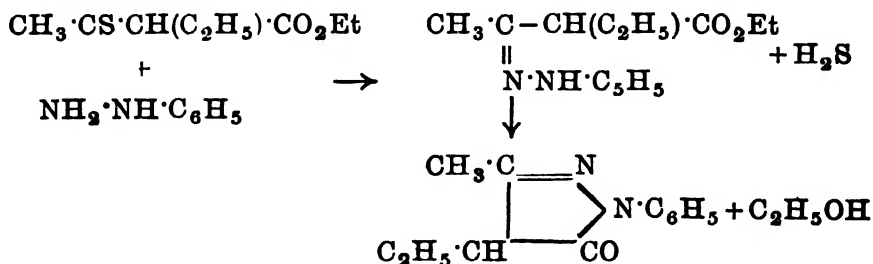
## Thioketonic Esters. Part IV.

By SUSIL KUMAR MITRA.

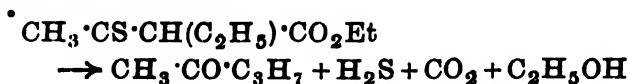
Ethylthioacetoacetate on alkylation yielded *S*-ethers (Mitra, *J. Indian Chem. Soc.*, 1933, 10, 71) which did not further react with sodium. Dialkyl derivatives could not therefore be directly obtained and the effect of C:S group on the second hydrogen atom of the reactive methylene group could not be studied. The *C*-alkyl derivative ( $\text{CH}_3 \cdot \text{CS} \cdot \text{CHEt} \cdot \text{COOEt}$ ) was, however, synthesised by the action of hydrogen sulphide on ethyl  $\alpha$ -ethylacetoacetate (*cf.* Mitra, *loc. cit.*).



This compound behaved both as a thiol, as evidenced by the decolourisation of alcoholic iodine and the formation of a lead salt, and also as a thioketone because on treatment with phenylhydrazine it yielded 1-phenyl-3-methyl-4-ethyl-5-ketopyrazolone by loss of hydrogen sulphide:

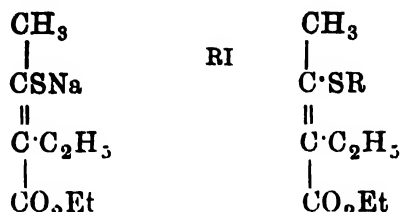


The compound on boiling with dilute hydrochloric acid evolved sulphuretted hydrogen and carbon dioxide and methylpropylketone was detected in the solution.



This compound like ethyl thioacetoacetate reacted with sodium with evolution of hydrogen and formation of a sodium derivative.

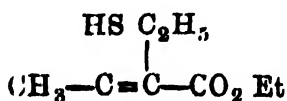
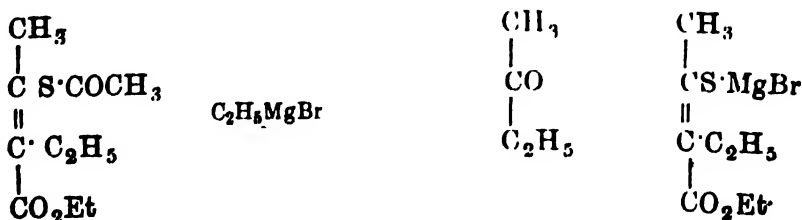
Alkyl derivatives, prepared by the action of alkyl halides on the sodium derivative, appear to be *S*-ethers.



The absence of thiol group in these compounds was confirmed as they could neither decolourise alcoholic solution of iodine nor could give lead salt and the absence of a thioketonic group was inferred from their incapability to react normally with phenylhydrazine in the cold with evolution of sulphuretted hydrogen. Phenylhydrazine at higher temperatures reacted with these compounds with evolution of mercaptans and formation of 1-phenyl-3-methyl-4-ethyl-5-ketopyrazolone. On boiling with dilute acids these compounds evolved mercaptans and carbon dioxide. These facts assert the mobile nature of the sulphur atom in the  $\beta$ -position to the carbethoxy group.

Ethyl ethylthioacetoacetate furnished acetyl and benzoyl derivatives. The acylated products do not contain any thiol group. They react with phenylhydrazine forming symmetrical acetyl- and benzoyl-phenylhydrazine respectively and 1-phenyl-3-methyl-4-ethyl-5-ketopyrazolone. Thus it becomes conclusive that phenylhydrazine primarily knocked off the acyl groups and then reacted with the liberated ethyl ethylthioacetoacetate and formed the corresponding pyrazolone.

The action of Grignard's reagent supports such a structure for the acyl derivatives. The acetyl derivative, on treatment with ethylmagnesium bromide, furnished methylethylketone and ethyl ethylthioacetoacetate was regenerated.



It can safely be concluded that the effect of the thioketonic group on the second hydrogen atom of the methylene group in close proximity is exactly identical with that of the first.

#### EXPERIMENTAL.

*Ethyl ethylthioacetoacetate*.—Ethyl ethylacetoacetate (100 g.) was dissolved in alcohol (200 c. c.) saturated with hydrochloric acid gas at 0° and sulphuretted hydrogen was slowly bubbled for 8 hours at 0°. The whole mass was then treated with excess of ice-cold water and the oil was extracted with ether. The ethereal solution was dried and the red oil obtained after removal of ether was diluted to three times the volume with rectified spirit. Freshly prepared lead oxide was added to the solution under constant stirring at 0°. The precipitated lead salt was decomposed with dilute hydrochloric acid, when an emulsion was obtained which was extracted with ether, dried and distilled after removal of the solvent. A red oil (b. p. 85°/14 mm) was obtained in 80% yield. (Found: C, 54·9; H, 8·1; S, 18·1.  $C_8H_{14}O_2S$  requires C, 55·1; H, 8·04; S, 18·31 per cent).

*1-Phenyl-3-methyl-4-ethyl-5-ketopyrazolone*.—Ethyl ethylthioacetoacetate (5 g) was treated with phenylhydrazine (2·5 g), when sulphuretted hydrogen began to evolve briskly. When the reaction was moderated the whole mass was heated on a water bath for 2 hours. The product was washed several times with petroleum ether and finally crystallised from methyl alcohol in needles, m. p. 108°. (Found: N, 13·51.  $C_{12}H_{14}ON_2$  requires N, 13·81 per cent).

*Ketone hydrolysis of ethyl ethylthioacetoacetate*.—Ethyl ethylthioacetoacetate (15 g.) was boiled with dilute sulphuric acid (10%, 100 c. c.) and after 5 hours when no more sulphuretted hydrogen or carbon dioxide was evolved; the aqueous residue was repeatedly extracted with ether and the liquid obtained after removal of the solvent was found to be methylpropylketone; the semicarbazone, m. p. 100°, the melting point not being depressed when mixed with an authentic specimen.

*Ethyl  $\beta$ -ethylmercapto- $\alpha$ -ethylcrotonate*.—Molecular sodium (2·5 g.) was added under ice-cooling to ethyl ethylthioacetoacetate (20 g.) in dry benzene (50 c.c.) and after 3 hours, ethyl bromide (15% more than theoretical) was added. The whole mass was then refluxed for 6 hours on a water-bath, poured into water and the benzene layer collected. The oil obtained after removing benzene was

distilled at 95°/14 mm., yield 60%. (Found: C, 60·3; H, 9·1; S, 15·1.  $C_{10}H_{18}O_2S$  requires C, 59·4; H, 8·9; S, 15·8 per cent).

*Ethyl  $\beta$ -isobutylmercapto- $\alpha$ -ethylcrotonate.*—Ethyl ethylthioacetoacetate (5 g.) dissolved in benzene (20 c. c.) was added slowly to an alcoholic solution of sodium ethoxide (0·6 g. sodium in 10 c.c. alcohol) and after 3 hours isobutyl iodide (6 g.) was added. The oil obtained as before was distilled after removal of benzene in vacuum and the fraction, b.p. 100°/15 mm. collected, yield 4 g. (Found: C, 62·38; S, 13·6.  $C_{12}H_{22}O_2S$  requires C, 62·6; S, 13·9 per cent).

*Ketone hydrolysis of the alkylated products.*—Ethyl  $\beta$ -ethylmercapto- $\alpha$ -ethylcrotonate (10 g.) was heated with sulphuric acid (10%, 75 c.c.) and the condenser was connected to two bubblers containing alcohol. The heating was continued till no more mercaptan was detected by lead acetate paper. The alcoholic solutions were then treated with excess of alcoholic solution of iodine, diluted with water and extracted by means of ether. The oil obtained after removal of ether was identified as diethyl disulphide (b.p. 152°). (Found: S, 51·9. Calc.: S, 52·41 per cent).

*Action of phenylhydrazine on alkylated products*—Ethyl  $\beta$ -ethylmercapto- $\alpha$ -ethylcrotonate and phenylhydrazine were heated to boiling on the sand-bath in a test tube, the test tube being connected with an alcoholic washer. After 1 hour the alcohol in the washer was treated with excess of alcoholic solution of iodine and the oil obtained after diluting with excess of water was identified to be diethyl disulphide. The residue in the test tube after washing with petroleum ether furnished 1-phenyl-3-methyl-4-ethyl-5-ketopyrazolone, m. p. 108°, the mixed m.p. with an authentic specimen was unchanged.

*Ethyl  $\beta$ -acetylmercapto- $\alpha$ -ethylcrotonate.*—Ethyl ethylthioacetoacetate (20 g.) was treated with molecular sodium (2·5 g.) in benzene (100 c.c.) under ice-cooling and after 3 hours acetyl chloride (10 g.) was added under vigorous shaking and the mixture heated on the water-bath for 6 hours. The solution was poured into excess of water and the benzene repeatedly washed with water. On removing the solvent the product distilled at 105°/12 mm. (Found: C, 55·1; H, 7·0; S, 14·3.  $C_{10}H_{16}O_3S$  requires C, 55·5; H, 7·4; S, 14·81 per cent). The same acetyl derivative was obtained by the action of thioacetic anhydride (70 g.) and pyridine (1 c.c.) upon ethyl thioacetoacetate (20 g.).

*Ethyl  $\beta$ -benzoylmercapto- $\alpha$ -ethylcrotonate.*—Ethyl ethylthioacetoacetate (20 g.) and sodium (2·5 g.) reacted with benzoyl chloride (15 g.)



in a manner similar to the preceding experiment and furnished an oil, b.p.  $185^{\circ}/18$  mm. (Found: C, 64.1; S, 11.9.  $C_{15}H_{18}O_3S$  requires C, 64.7; S, 11.60 per cent).

*Action of phenylhydrazine on acetylated product.*—Ethyl  $\beta$ -acetylmercapto- $\alpha$ -ethylcrotonate was treated with phenylhydrazine in the cold, when the mixture gradually became warm and the mass solidified with evolution of sulphuretted hydrogen. When no more sulphuretted hydrogen was evolved the product was extracted with ether and crystallised from methyl alcohol, m.p.  $125^{\circ}$ . It is identical with acetylphenylhydrazine. (Found: N, 18.75. Calc.: N, 18.71 per cent). The ether extract left a viscous oil after removal of ether and the oil on heating on the water-bath for 3 hours furnished 1-phenyl-3-methyl-4-ethyl-5-ketopyrazolone, m.p.  $108^{\circ}$ .

*Action of phenylhydrazine on benzoylated product.*—Ethyl  $\beta$ -benzoylmercapto- $\alpha$ -ethylcrotonate was treated with phenylhydrazine, when heat was developed and the mass solidified. *sym*-Benzoylphenylhydrazine was isolated as in the previous case, m.p.  $168^{\circ}$ ; the mixed m.p. with a known sample was unchanged; yield theoretical.

*Action of ethylmagnesium bromide on ethyl  $\beta$ -acetylmercapto- $\alpha$ -ethylcrotonate.*—Ethyl  $\beta$ -acetylmercapto- $\alpha$ -ethylcrotonate (15 g.) dissolved in ether (100 c.c.) was added drop by drop over magnesium-ethyl bromide prepared by dissolving magnesium (2.5 g.) in ethyl bromide (15 g.) cooled in ice and the mixture left overnight. The granular white precipitate was filtered and acidified with dilute hydrochloric acid and the oil obtained was extracted with ether, the ethereal extract dehydrated and distilled at  $85^{\circ}/14$  mm. It was identified to be ethyl ethylthioacetoacetate. (Found: S, 17.9. Calc.: S, 18.3 per cent).

The ethereal filtrate in the above experiment furnished a liquid which gave a semicarbazone, m.p.  $135^{\circ}$  identical with that of methyl-ethylketone.

My sincere thanks are due to Sir P. C. Ray for his keen interest in this investigation and also for the facilities granted.



# The Behaviour of the Hydrochlorides of Organic Bases towards Chlorauric Acid. On the Constitution of the Abnormal Auric Chloride Complexes.

BY DINESH CHANDRA SEN.

Fenner and Tafel (*Ber.*, 1899, 32, 3220) have found that the hydrochlorides of piperidine, quinoline, isopropylamine and 2:5-dimethylpyrrolidine react with auric chloride in two different ways under different conditions forming two types of complex compounds, one being represented by the formula  $X(AuCl_4)$  (I) while the other is represented by  $X_2(AuCl_3)$  (II), where X stands for the organic basic radical. The first type of compounds is produced when the reaction takes place in aqueous medium while the second type is generated in alcoholic solution containing free hydrochloric acid. Compounds of the formula  $X(AuCl_4)$  are evidently similar to those of the alkali metals, but chlorides of sodium, potassium, etc., produce no complexes of the second type. The latter type of complexes can be represented by either of the following three constitutional formulæ: (1)  $X_2(AuCl_3)$ , (2)  $X(AuCl_4) \cdot XCl$ , (3)  $AuCl_3 \cdot 2 XCl$ . Formula (1) (Fenner and Tafel, *loc. cit.*) can of course be explained on the basis of Werner's theory assuming the valency of gold to be three, the valency of the two extra chlorine atoms being satisfied by the electropositive basic radicals; but then the co-ordination number becomes five which is rather unusual in common auric complexes. Moreover, it is not possible to explain the chemical and physical properties of these compounds on the basis of the above formula.

The present investigation was undertaken with a view to throw light on the constitution of these complexes by determination of the molecular conductivity and molecular volume of some of the typical complexes. Incidentally, complexes of different organic bases other than those used by Fenner and Tafel (*loc. cit.*) have also been prepared.

## EXPERIMENTAL.

*Preparation of the compounds.*—Compounds of the types of  $X(AuCl_4)$  and  $X_2(AuCl_3)$  have been prepared exactly by following the method of Fenner and Tafel (*loc. cit.*), only chlorauric acid has been used in place of auric chloride. The hydrochlorides of organic bases employed were quinoline, piperidine, ethylamine, benzylamine and trimethylamine. The complexes of the first two were already prepared by the above investigators who were, however, unable to prepare

compounds of the type  $X_2(AuCl_5)$  with the hydrochlorides of some of the organic bases. The author also failed to prepare compounds of this type with benzylamine and trimethylamine hydrochlorides, only the normal compounds being prepared both in aqueous and alcoholic solutions. Ethylamine hydrochloride, however, behaved like the hydrochlorides of quinoline, piperidine, etc., and an abnormal compound was obtained from alcoholic solution containing hydrochloric acid. The formation of these two types of complexes does not depend on the concentration of the reactants; it entirely depends upon the medium. The same normal salt,  $X(AuCl_4)$  always formed in aqueous medium by varying the concentration of the reactants, but the maximum yield was obtained by treating chloroauric acid with molecular proportions of the basic hydrochlorides. Similarly the same compound  $X_2(AuCl_5)$  formed by varying the concentration of the reactants in alcoholic hydrochloric acid medium, maximum yield being obtained with twice the molecular proportion of basic hydrochloride per molecule of chloroauric acid. The second type of compounds was also obtained by heating an alcoholic solution of  $X(AuCl_4)$  in presence of hydrochloric acid. The composition of the complexes are given in Table I.

TABLE I.

Compounds.	Formulae.	M. p.	Found.	Theoretical
Quinolinium auric chloride	$C_9H_7N^+(AuCl_4^-)$	236°	Au, 41·98% Cl, 29·85	42 % 30·28
Quinolinium auric chloride-quinolinium chloride	$C_9H_7N(AuCl_4) \cdot C_9H_7NCl$	180°	Au, 31·12 Cl, 27·76	31·05 27·97
Piperidinium auric chloride	$C_5H_{12}N(AuCl_4)$	206°	Au, 46·38 Cl, 33·28	46·35 33·41
Piperidinium auric chloride-piperidinium chloride	$C_5H_{12}N(AuCl_4) \cdot C_5H_{12}NCl$	183°	Au, 36·02 Cl, 32·46 N, 5·13	36·05 32·48 5·12
Ethylammonium auric chloride	$C_2H_5N(AuCl_4)$	195°	Au, 50·89 Cl, 35·92	51·17 36·09
Ethylammonium auric chloride-ethylammonium chloride	$C_2H_5N(AuCl_4) \cdot C_2H_5NCl$	70°	Au, 42·6 Cl, 37·78	42·2 38·05
Benzylammonium auric chloride	$C_7H_{10}N(AuCl_4)$	168°	Au, 44·19 Cl, 31·98	44·07 31·77
Trimethylammonium auric chloride	$C_3H_{10}N(AuCl_4)$	220°	Au, 49·4 Cl, 35·42	49·37 35·6

\* The melting point of  $C_5H_{12}N(AuCl_4) \cdot C_5H_{12}NCl$ , recorded by Fenner and Tafel (loc. cit.) was 170°, much lower than the actual melting point of the substance probably due to the presence of some impurities in the compound prepared by these authors.

*Determination of conductivity and molecular volume.*—The following tables contain the results of specific resistances of the complexes of types  $X(\text{AuCl}_4)$  and  $X_2(\text{AuCl}_5)$  and of an equimolecular mixture of  $X(\text{AuCl}_4)$  and  $\text{XCl}$  and also of the molecular volumes of  $\text{XCl}$ ,  $X(\text{AuCl}_4)$  and  $X_2(\text{AuCl}_5)$  when X represents either a piperidinium or a quinolinium radical.

TABLE II.

*Base quinoline.*

Sp. resistances observed in alcoholic solution at 31°.

Conc. in m. moles/litre ...	5	2.5	1.25	0.625	0.3125
Quinolinium auric chloride-quinolinium chloride ...	211	352	583	949	1445
Equimol. mixture of quinolinium auric chloride and quinolinium chloride	212	351	582	949	1445

TABLE III.

*Base piperidine.*

Sp. resistances observed in alcoholic solution at 25°.

Conc. in m. moles/litre ...	10	5	2.5	1.25
Piperidinium auric chloride-piperidinium chloride .	137	238	407	705
Equimol. mixture of piperidinium auric chloride and piperidinium chloride .	141	239	408	706

TABLE IV.

*Base quinoline.*

Molecular volumes at 25°. Sp. gr. determined in xylene medium.

	Auric chloride.	Quinolinium chloride.	Auric chloride & quinolinium chloride calc.	Quinolinium auric chloride obs.	Quinolinium auric chloride & quinolinium chloride.	
					calc.	obs.
Sp. gr.	4.3	1.45	—	1.91	—	1.762
Mol. vol.	70	114.1	184.1	245	359.1	860

TABLE V.

*Base piperidine,*

Molecular volumes at 25°. Sp. gr. determined in xylene medium.

	Auric chloride.	Piperidi- nium chloride.	Auric chloride and pi- peridi- nium chloride calc.	Piperidi- nium auric chloride observed.	Piperidinium auric chloride and piperidinium chloride.	
					calc.	obs.
Sp. gr.	4.3	1.26	—	1.837	—	1.679
Mol. vol.	70	95	165	231.3	326.3	325.5

## DISCUSSION.

Compounds of the type  $X_2(AuCl_5)$  are unstable in an aqueous or acetone medium. Though they are soluble and fairly stable in cold alcohol, they decompose in hot alcoholic medium,  $X(AuCl_4)$  being one of the products of decomposition in each case. They are very stable in alcohol containing free hydrochloric acid even at the boiling temperature. When the yellow salts  $X_2(AuCl_5)$  were treated with a little acetone, they gradually turned white, the white crystals were separated, and identified to be the corresponding basic hydrochlorides which being sparingly soluble in acetone separated out, while the more soluble  $X(AuCl_4)$  remained in a state of solution. On the other hand, when the salts were treated with water, the more soluble basic hydrochloride went into solution leaving the less soluble normal salt in the undissolved state. The separation of the two components under these two conditions was nearly quantitative. It was also possible to make the two components  $X(AuCl_4)$  and  $XCl$  combine together by warming the equimolecular quantities of the two salts in alcoholic hydrochloric acid.

The molecular weights of some of the salts were determined by the previous authors (*loc. cit.*) in alcoholic solution by the ebullioscopic method and it was noticed that in the case of piperidinium chloride and piperidinium auric chloride, the observed molecular weights were in agreement with their theoretical values within the limits of experimental error, but that of the abnormal salt,  $X_2(AuCl_5)$  was found to be nearly half of the actual value as calculated from

the formula. This might probably be due to the decomposition of the complex salt into the constituent molecules because of its unstability under the experimental conditions.

\*The easy decomposition of the  $\text{AuCl}_3, 2\text{XCl}$  into the two components  $\text{X} \cdot \text{AuCl}_4$  and  $\text{XCl}$  even by the simple addition of water or acetone or molecular weight data cannot be explained by  $\text{X}_2(\text{AuCl}_5)$ . From our results on molecular volumes and specific resistances it is evident that the compounds  $\text{X}_2(\text{AuCl}_5)$  should be represented as a molecular compound of the type  $\text{X}(\text{AuCl}_4), \text{XCl}$ , because it was noticed that the formation of complexes like  $\text{C}_9\text{H}_8\text{N}(\text{AuCl}_4)$  and  $\text{C}_5\text{H}_{12}\text{N}(\text{AuCl}_4)$  were attended by an expansion in volume, nearly 33% in the first case and 40% in the second, whereas the formation of  $\text{C}_5\text{H}_{12}\text{N}(\text{AuCl}_4) \cdot \text{C}_5\text{H}_{12}\text{NCl}$  or the corresponding quinolinium chloride derivative was not attended with any alteration in volume. When the molecular volumes and specific resistances of  $\text{XCl}$  and  $\text{X}(\text{AuCl}_4)$  are added, the values are found to be equal to those of  $\text{X}_2(\text{AuCl}_5)$  complexes.

Thus it is definitely established that of the two molecules of  $\text{XCl}$  linked to each molecule of  $\text{AuCl}_3$ , in  $\text{X}_2(\text{AuCl}_5)$  or  $\text{AuCl}_3, 2\text{XCl}$ , one forms a complex  $\text{X}(\text{AuCl}_4)$  which itself forms a molecular compound with the second molecule of  $\text{XCl}$ .

#### SUMMARY

1. The normal and abnormal salts of auric chloride and piperidinium, quinolinium, and ethylammonium salts have been prepared. The normal salts only have been obtained in the case of benzylammonium and trimethylammonium chlorides.

2. Complexes of the type  $\text{X}_2(\text{AuCl}_5)$  named as abnormal auric chlorides of gold have been shown to be molecular compounds of the type  $\text{X}(\text{AuCl}_4), \text{XCl}$ .

My thanks are due to Sir P. C. Rây for the kind interest he took during the investigation





## The Adsorbabilities of the Ions.

By K. S. GURURAJA DOSS.

Mukherjee (*Trans. Faraday Soc.*, 1921, **16** 103) has proposed an interesting theory explaining the origin and the neutralisation of the charge on a colloidal particle. The origin of the charge is supposed to be due to the adsorption of ions by the atoms in the surface by virtue of their chemical affinity. On account of this charge, ions of the opposite sign are drawn near the surface. Among them, those which have their kinetic energy less than  $W$ , the energy required to separate the ion from the surface are considered as not "free". The number of such "bound" ions determines the diminution in the charge of the surface. On the basis of the above assumptions, an equation connecting  $\theta_2$ , the fraction of the original charge left unneutralised after electrical adsorption, with  $C$ , the concentration of the ion (getting adsorbed) in the bulk solution, has been derived for the idealised case in which "there is no chemical affinity acting between the ions of opposite sign." The equation so deduced has been tested and found to be of the right form to express the experimental results. An attempt is made in this paper to discuss the significance of the constants in the equations worked out.

It has been shown (Mukherjee, *loc. cit.*) that

$$1 - \theta_2 = k_0 \left\{ C \cdot \frac{n_2 - n_1}{n_1} \cdot \theta_2 + C \theta_2^2 \right\}$$

where  $k_0 = \frac{k_4}{k_1} n_2 \cdot u \cdot e^{W/kT}$

(Mukherjee's expression for  $k_0$  contains the negative exponent, which is evidently a slip). The symbols employed have the following significance.

$1 - \theta_2$  = Fraction of the total charge on the surface neutralised.

$n_1$  = Valency of the ions chemically adsorbed.

$n_2, C, u$  = Valency, concentration, and mobility respectively of the oppositely charged ions in the liquid in contact with the surface.

$k$  = Boltzmann constant.

$T$  = Absolute temperature.

$W$  = The energy required to separate an ion from an oppositely charged surface.

$k_4, k_1$  = Constants for the significance of which see the original paper by Mukherjee (*loc. cit.*).

As Mukherjee (*loc. cit.*) points out,  $k_4$  contains the " $Nn_1$ " term. Splitting it and collecting the universal constants together, we get,

$$1 - \theta_2 = k_5 \cdot u e^{W/kT} \cdot C \{n_2(n_2 - n_1)\theta_2 + n_1 n_2 \theta_2^2\}$$

$$\text{where } k_5 = \frac{k_4}{Nn_1} = \frac{k_0}{u e^{W/kT} \cdot n_1 n_2}$$

This constant  $k_5$  depends only on the spatial distribution of charge on the surface and on the kinetic factors other than the mobility, determining the collision frequency.

When  $W$  is much less than  $kT$ , we can put,

$$\frac{1}{C} = k_5 \cdot \frac{\{n_2(n_2 - n_1)\theta_2 + n_1 n_2 \theta_2^2\}}{1 - \theta_2}$$

The right hand side expression is the reciprocal of the concentration at which a fraction  $1 - \theta_2$  of the total charge is neutralised and hence can be used as a measure of the adsorbability of the ion.

We shall now proceed to work out the theoretical lyotropic series. Let  $A_m, A_b, A_t$  and  $A_q$  be the adsorbabilities of monovalent, divalent, trivalent, and quadrivalent ions respectively. Let  $u_m, u_b, u_t$  and  $u_q$  be the corresponding mobilities.

If  $\theta_2$  is very nearly equal to 1, we get,  $A < u n_2^2$

$$\therefore A_m : A_b : A_t : A_q :: u_m : 4u_b : 9u_t : 16u_q$$

If  $\theta_2$  is very nearly zero,  $A < u(n_2^2 - n_1 n_2)$

$$\therefore A_m : A_b : A_t : A_q :: 0 : u_m : 2u_b : 6u_t : 12u_q$$

If  $\theta_2 = \frac{1}{2}$ ,  $A < u(2n_2^2 - n_1 n_2)$

$$\therefore A_m : A_b : A_t : A_q :: u_m : 6u_b : 15u_t : 28u_q$$

Table I gives the theoretical adsorbabilities of various ions as worked out on the above basis. Thus we arrive at the lyotropic series:

For $\theta_2 = 1$ ,	Th > Al > H > Ba > Sr > Ca > Mg > Cs > Rb > K > Ag > Na > Li.
$\theta_2 = \frac{1}{2}$ ,	Th > Al > Ba > H > Sr > Ca > Mg > Cs > Rb > K > Ag > Na > Li.
$\theta_2 = 0$ ,	Th > Al > Ba > Sr > Ca > Mg > H > Cs > Rb > K > Ag > Na > Li.

We shall now proceed to work out the empirical lyotropic series from the data cited by Mukherjee (*loc. cit.*). As the data are limited to mono- and divalent ions we shall consider only those cases. From the general formula for adsorbability,

$$\frac{A_m}{A_b} = \frac{\theta_2}{2 + 2\theta_2} \cdot \frac{u_m}{u_b}.$$

Also we know,

$$k_5 = \frac{k_0}{ue^{W/kT}} \cdot \frac{1}{n_1 n_2} \quad \therefore u = \frac{k_0}{k_5} \cdot \frac{1}{e^{W/kT}} \cdot \frac{1}{n_1 n_2}.$$

If  $W$  is much less than  $kT$ ,  $\frac{u_m}{u_b} = \frac{2k_{0m}}{k_{0b}}$  [ $k_{0m}$  and  $k_{0b}$  are the values of  $k_0$  for the monovalent and the divalent ions respectively]

$$\therefore \frac{A_m}{A_b} = \frac{2k_{0m}}{k_{0b}} \cdot \frac{\theta_2}{2 + 2\theta_2} \quad \therefore A_m : A_b :: k_{0m} : k_{0b} \cdot \frac{2 + 2\theta_2}{\theta_2}.$$

$$\text{If } \theta_2 = 0, \quad A_m : A_b :: k_{0m} : \infty k_{0b}.$$

$$\text{If } \theta_2 = \frac{1}{2}, \quad A_m : A_b :: k_{0m} : 3 k_{0b}.$$

$$\text{If } \theta_2 = 1, \quad A_m : A_b :: k_{0m} : 2 k_{0b}.$$

Table II gives the experimental values of the adsorbabilities calculated by the above equations. Thus the empirical lyotropic series works out to be

for  $\theta_2=1$ ,  $H, Hg > Ba > K > Na$

$\theta_2=\frac{1}{2}$ ,  $H, Ag > Ba > K > Na$

$\theta_2=0$ ,  $Ba \gg H, Ag > K > Na$ .

Thus we find that in the case of  $\theta_2=\frac{1}{2}$  the theoretical series gives  $Ba > H$  and the empirical series gives the order  $H > Ba$ . So, it would be of interest to compare the theoretical and the empirical values of the relative adsorbabilities of H and Ba over the whole range of the values of  $\theta_2$ .

$$\text{Now } A_H / A_{Ba} = \frac{u_H}{2u_{Ba}} \cdot \frac{\theta_2}{1 + \theta_2} \quad \text{and}$$

(Theoretical).

$$A_H / A_{Ba} = \frac{k_{oH}}{k_{oBa}} \cdot \frac{\theta_2}{1 + \theta_2}$$

(Experimental).

Table III gives the empirical and the theoretical values of  $A_H / A_{Ba}$  as calculated from the above formula. The theory and the experiment agree only at  $\theta_2=0$ . As  $\theta_2$  increases gradually to unity, the deviation also progressively increases. The maximum disparity is got when  $\theta_2=1$  (i.e., in the region of dilute solutions where maximum agreement is to be expected). Throughout the H ion is adsorbed to a greater extent than what is predicted by the theory. It is seen in particular that between the limits  $\theta_2=0.38$  and  $\theta_2=0.54$ , the theoretical curve indicates  $Ba > H$ , whereas the experimental curve shows the reverse. No doubt the theoretical curve has been derived on the assumption  $W \ll kT$ . Even if this simplification is not made it only makes the agreement between theory and experiment worse.

These results should not be interpreted as invalidating the general theory forwarded by Mukherjee. On the other hand, they hint at other factors which may be at play as has already been envisaged by the author of the theory. First, the interaction of the H ions with the primarily adsorbed anions is mainly of a chemical nature. The potential energy  $A$ , determining the adsorbability has to be considered in this case as consisting of the sum of  $W$ , the electrical potential energy which has been formulated for the idealised case and  $B$ , in which the potential energy arising out of all other types of interactions (such as deformation) is included. Secondly, the electrical adsorption of a divalent ion is in some respects different

from that of the univalent ion. This becomes clear when one considers the mutual repulsion between the two univalent kations when they are simultaneously electrically adsorbed by a divalent anion which is absent when a divalent kation is adsorbed; again considering the electrical adsorption by a primarily adsorbed univalent anion, it is seen that the divalent kation brings about a reversal of charge, an effect absent in the case of univalent kations. \*Lastly, the primarily adsorbed ions cannot definitely be known. Divalent (presumably the silicate ions) and univalent ions may both be present in this particular case. These factors account for the disparity between the theory and the experimental data, and, the existence of a general parallelism between theory and observation even when H ions are taken into consideration possibly indicates that the potential energy  $A$  (i.e.,  $W + B$ ) is the main factor in determining the adsorbability of the ions.

TABLE I\*.

Ion.	Mobility	Adsorbability for		
		$\theta_2 = 1$	$\theta_2 = \frac{1}{2}$	$\theta_2 = 0$
H	314.0	314.0	314.0	0
Ca	68.0	68.0	68.0	0
Rb	67.5	67.5	67.5	0
K	64.6	64.6	64.6	0
Ag	54.0	54.0	54.0	0
Na	43.4	43.4	43.4	0
Li	33.3	33.3	33.3	0
Ba	55.4	222.0	332.0	111.0
Sr	51.9	208.0	311.0	104.0
Cs	51.9	208.0	311.0	104.0
Mg	45.9	184.0	275.0	92.0
Al	40.0	360.0	600.0	240.0
Th	28.5	376.0	658.0	282.0

TABLE II\*.

Ion.	$k_0 \times 100.$	Adsorbability for		
		$\theta_2 = 1.$	$\theta_2 = \frac{1}{2}.$	$\theta_2 = 0$
Na	0.76	0.76	0.76	0.76
K	0.87	0.87	0.87	0.87
H	5.9	5.9	5.9	5.9
Ag	5.9	5.9	5.9	5.9
Ba	1.63	3.26	1.9	$\infty$

TABLE III.

		0.00	0.1	0.3	0.5	0.8	1.0
$A_H / A_{Ba}$	... 0.00	0.26	0.66	0.95	1.27	1.42	
(Theoretical)							
$A_H / A_{Ba}$	... 0.00	0.33	0.84	1.21	1.61	1.81	
(Experimental)							

## SUMMARY.

Certain data on ionic adsorption have been considered in view of Mukherjee's theory; the adsorbability of the H ion as compared with that of the Ba ion is shown to be higher than what the formulation for the idealised case of electrical adsorption would predict which hints at importance of factors such as deformation in the consideration of the adsorbability of the H ion.

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\* Tables I and II contain only the relative adsorabilities at particular values of  $\theta_2$ . The absolute values cannot be determined as  $k_1$  is unknown.

## The Kinetics of Slow Coagulation. Part I.

By D. N. GHOSH.

It is well known that Smoluchowski's equation for the rapid coagulation of a colloid proves unsatisfactory when it is extended to cases of slow coagulation. The process of slow coagulation of a colloid is generally autocatalytic in nature where the rate of coagulation is given by the characteristic S-shaped curves.

An examination of the data obtained by Ishizuka (*Z. physikal. Chem.*, 1913, **83**, 97), Gann (*Koll. Chem. Beih.*, 1916, **8**, 65), Lottermoser (*Kolloid Z.*, 1914, **15**, 145) and others in the light of Smoluchowski's theory, showed that the autocatalytic nature of a coagulation process cannot be explained on the basis of the above theory. Even in cases where the coagulation process has lost its autocatalytic nature, marked divergences from Smoluchowski's theory have been observed. Thus ultra-microscopic measurements of the rate of coagulation by Steacie (*J. Phys. Chem.*, 1930, **34**, 1850), Kruyt and van Arkel (*Kolloid Z.*, 1923, **32**, 29) with different colloids have shown that although the process is not autocatalytic in nature, the rate of coagulation is distinctly slower than that required by Smoluchowski's theory. Similar divergences become apparent from an examination of the experimental data of Desai (*Trans. Faraday Soc.*, 1928, **24**, 181).

Westgren and Reitstotter (*J. Phys. Chem.*, 1922, **26**, 5371) have pointed out that Smoluchowski's theory should apply only to monodisperse sol. According to them the divergences from the theory are due mainly to (i) polydisperse nature of the colloid, and, (ii) presence of traces of electrolytes in the colloid. In the present paper using Odén's sulphur sol it has been shown that Smoluchowski's theory breaks down even when the sol is monodisperse; the sol is free from traces of ignogenic impurities, and is so dilute that its coagulation is no longer autocatalytic.

### EXPERIMENTAL.

The sample of sulphur sol was prepared by the method given by Bassett and Durrant (*J. Chem. Soc.*, 1931, 2933) and from this a sample of monodisperse sol was obtained by the following method. The sol was just made turbid by the addition of a few drops of 2N-NaCl, allowed to stand for sometime, after which the coagulum

was separated by filtration through a Zsigmondy membrane filter. This process was repeated several times and the coagulum obtained during the last fraction was dissolved in distilled water when a clear sol was obtained. It has been shown by Odén (*Kolloid Z.*, 1911, 8, 186) that the colloid obtained by the above method is a monodisperse sol.

The tyndallmeter described by the author in a previous paper (*J. Indian Chem. Soc.*, 1933, 9, 592) has been used for measuring the rate of coagulation of the monodisperse sol using potassium chloride as the coagulating electrolyte. To a measured volume of the sol a known amount of electrolyte was added and this mixture was used on the tyndallmeter. The intensity of the scattered beam was measured at definite intervals of time; the experimental values have been plotted in Figs. 1 and 2. From these figures the times corresponding to the same stage of coalescence of the sol have been obtained and are given in Tables I and II.

FIG. 1.

*Light scattering—time curves for conc. sol*

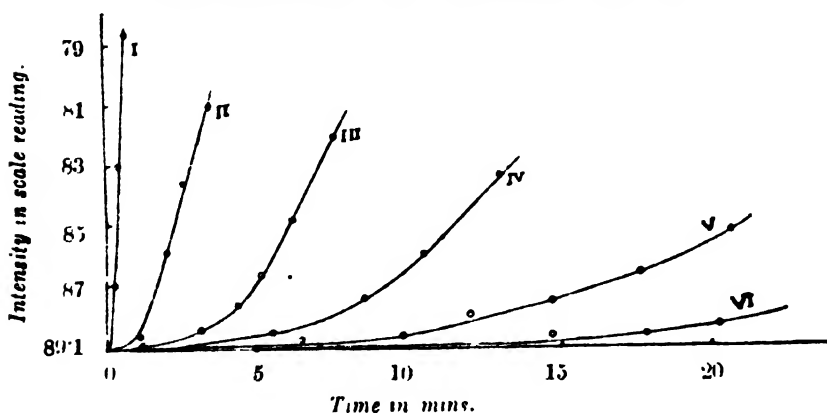


FIG. 2.

*Light scattering—time curves for dil. sol.*

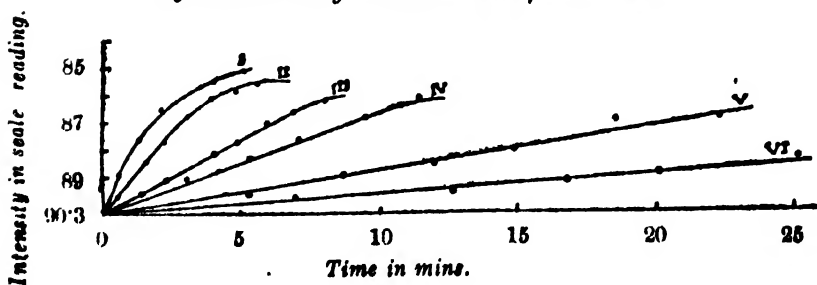




TABLE I.

Sol concentration = 40 mg. of sulphur per litre.

Curves	I.	II.	III.	IV	V	VI.						
Electrolyte conc. m.m ls./liter →	110	87.5	75	70	65	60	Ratio values.					
Intensity (scale readings).	<i>T</i> (sec.)	<i>T</i> <sub>1</sub>	<i>T</i> <sub>2</sub>	<i>T</i> <sub>3</sub>	<i>T</i> <sub>4</sub>	<i>T</i> <sub>5</sub>	<i>T</i> <sub>1</sub> / <i>T</i> .	<i>T</i> <sub>2</sub> / <i>T</i> .	<i>T</i> <sub>3</sub> / <i>T</i> .	<i>T</i> <sub>4</sub> / <i>T</i> .	<i>T</i> <sub>5</sub> / <i>T</i> .	
88.5	9	69	186	366	630	1212	7.6	20.6	40.6	70	134.6*	
88	12	80	274	456	780	1680	6.6	22.8	38	65	140	
87	14	99	290	570	996	...	7.0	20.7	40.7	71.1	...	
66	18	117	330	633	1146	...	6.5	18.3	35.1	63.6	...	
85	21	134	363	693	1270	...	6.4	17.3	33.2	60.4	...	
84	24	150	396	750	1404	..	6.2	16.5	31.2	58.5	...	

TABLE II.

Sol concentration = 6.5 mg. of sulphur per litre.

Curves →	I.	II.	III.	IV.	V.	VI.						
Electrolyte conc. m mols. litre. →	140	120	110	100	90	80	Ratio values.					
Intensity (scale reading).	<i>T</i> (sec.)	<i>T</i> <sub>1</sub>	<i>T</i> <sub>2</sub>	<i>T</i> <sub>3</sub>	<i>T</i> <sub>4</sub>	<i>T</i> <sub>5</sub>	<i>T</i> <sub>1</sub> / <i>T</i> .	<i>T</i> <sub>2</sub> / <i>T</i> .	<i>T</i> <sub>3</sub> / <i>T</i> .	<i>T</i> <sub>4</sub> / <i>T</i> .	<i>T</i> <sub>5</sub> / <i>T</i> .	
90	9	18	39	56	126	264	2	4.3	6.2	14.0	29.3	
89.5	22	42	96	136	306	690	1.9	4.3	6.1	13.9	31.1	
89	36	66	150	216	486	1080	1.9	4.2	6.0	13.5	30.0	
88.5	48	87	206	297	672	1464	1.8	4.3	6.1	14.0	30.5	
88	66	117	260	378	846	1890	1.8	4.0	5.7	12.8	28.0	
87.5	84	140	315	474	1080	...	1.7	3.8	5.6	12.3	...	

FIG. 3.



Simultaneously with the above measurements the absorption of light by the same sulphur sol has been followed by an experimental arrangement as shown in Fig. 3. A straight portion of the filament of 60 C. P. lamp was used as the light source. A parallel beam obtained by means of a system of lenses and a suitable aperture was rendered monochromatic by means of Zeiss light filter (designed for the blue mercury line 4359) and after passing through a double cell having two exactly similar compartments was photographed on Ilford process plates having a speed of H. D. 50. One of the compartments of the double cell contained only the colloid, while the other contained the colloid with the added amount of electrolyte. On the photographic plate a pair of lines is obtained; one is due to the beam which has passed through the clear sol, while the other is due to that passing through the sol—electrolyte mixture. The intensity of the pair of lines was next measured by a Zeiss micro photometer. A comparison of the intensities of the pair of lines enables one to determine the rate of coagulation of the colloid as the amount of light absorbed, on which depends the intensity of the lines, is proportional to the rate of coagulation of the sol. It was necessary, however, to keep the experimental conditions exactly the same in every case.

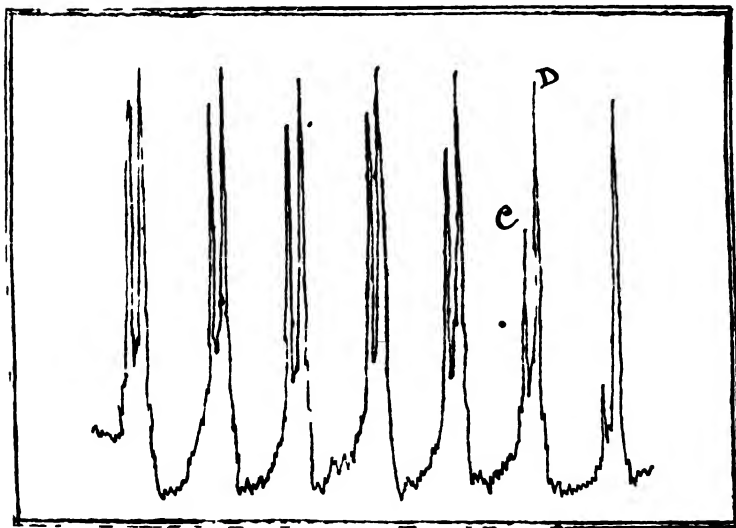
In Figs. 4 and 5 some of the photographs of the lines and copies of the prints obtained on the microphotograph are given.

FIG. 4.



It will be seen that corresponding to any pair of lines A and B, in Fig. 4, a curve with two adjacent peaks C and D (Fig. 5) are obtained on the print of the microphotometer. The difference of the heights between these peaks is proportional to the difference in the intensities of the lines A and B, which in its turn represents the difference in turbidity between the sols in the two compartments of the double cell. In the present experiments these differences between the heights of the peaks for a series of lines obtained at different intervals have been taken as a measure of the stage of coagulation of the sol.

FIG. 5.



To correct for any variation in the intensity at different parts of the straight filament used as the source and also for any difference in the thickness of the walls of the cell, an initial reading was taken when a sample of the same sulphur sol was placed in both the compartments of the double cell and this reading was used as the zero error for the subsequent measurements. The experimental values are given in the Table III.

FIG. 6.

Light absorption—time curve for conc. sol.

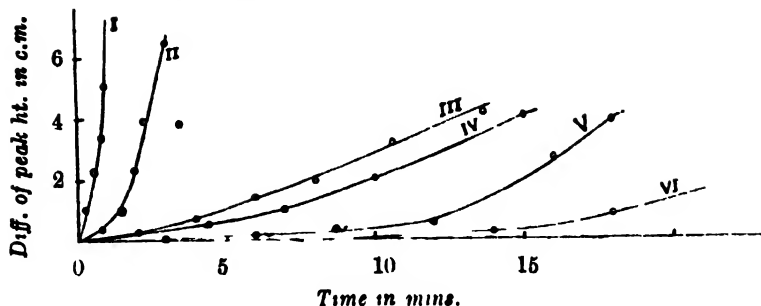


TABLE III.

Sol concentration = 40 mg. of sulphur per litre.

Curves →	I <sub>2</sub>	II.	III.	IV.	V.	VI.					
Electrolyte conc. in m. mols./litre. →	110	87.5	75	70	64	60					
Diff. in peak height.	240	200	175	165	155	145					
	Ratio values										
	$T$ (sec.)	$T_1$	$T_2$	$T_3$	$T_4$	$T_5$	$T_1/T$	$T_2/T$	$T_3/T$	$T_4/T$	$T_5/T$
0.5 cm.	12	56	228	312	606	990	4.4	19	28.5	58	62
1	16	90	306	420	800	1140	5.6	19	26.3	50	71
2	30	108	480	600	912	1320	3.6	16	20.0	30	44
3	42	126	636	750	1002	...	3.0	15	18.8	24	...
4	54	140	822	900	1080	...	2.6	15	17.0	20	...

Mukherjee and Papaconstantinou (*Phil Mag*, 1922, **44**, 305) have shown that according to Smoluchowski's theory the values of the ratios  $T_1/T$ ,  $T_2/T$ , etc., must be constant for every electrolyte concentration, where  $T$ ,  $T_1$ ,  $T_2$ , etc., are the respective times to reach the same stage of coalescence. An examination of the experimental data given in Table I shows that although Smoluchowski's theory applies fairly well during the earlier stages of the coagulation process, marked divergences are observed as the coagulation proceeds (*cf.* Mukherjee and Papaconstantinou, *loc cit.*; Westgren, *Ark. Matim. Astron. Fys.*, 1918, **13**, 1014; Mukherjee and Majumdar, *J. Chem. Soc.*, 1924, **125**, 704). Thus the values of  $T_1/T$  vary from 7.6 to 6.2, and those of  $T_3/T$  from 40.6 to 31.2.

Generally the values of the ratios  $T_1/T$ ,  $T_2/T$ , etc., are continuously decreasing, showing that the rate is becoming more and more rapid than that required by the theory. The present experiments with a monodisperse sol thus do not agree with the conclusion of Westgren and Reitstotter (*loc. cit.*) that the breakdown of the Smoluchowski's theory in the case of slow coagulation is due to the polydispersity of the colloid.

In Table II, are given the values obtained with a very dilute monodisperse sulphur sol. The rate of coagulation of the above sol can be clearly followed from Fig. 2. From the figure it is apparent that the S-shaped autocatalytic nature of the curve obtained with a fairly concentrated sol, disappears completely when the sol is made fairly dilute. From Table II we find that the values of the ratios  $T_1/T$ ,  $T_2/T$ , etc., are fairly constant when the coagulation is rapid, but show a distinct decrease as the rate of coagulation decreases. In the case of rapid coagulation, therefore, the results are in fair agreement with the theory, but when the case of slow coagulation is considered the above results clearly show that even when the sol is monodisperse and its rate of coagulation is not autocatalytic, Smoluchowski's theory does not hold strictly.

The sulphur sol used in the present experiments was fairly free from electrolytes as impurities. Preliminary experiments with a sample of the sol which was dialysed to remove practically all traces of electrolytes did not give any better values for the ratios. It appears, therefore, that divergences from Smoluchowski's theory cannot be satisfactorily explained as being due to traces of electrolytes in the sol.

The values for the ratios  $T_1/T$ ,  $T_2/T$ , etc., during the earlier stages of coagulation, as obtained from measurements with the microphotometer and given in Table III, were also not constant but they continually decreased showing as before, that the rate of coagulation is more rapid than that required by Smoluchowski's theory.

Mecklenburg (*Kolloid Z.*, 1916, 16, 97) using colloidal sulphur has shown that the intensity of the scattered beam is proportional to the concentration of the particles in the sol so long as the diameter of the particles does not exceed  $5\mu\mu$ . It is possible that the deviations observed towards the later stages of coagulation might be due to the size of the particles exceeding the Mecklenburg limit

of  $95\ \mu\mu$ , when the intensity of the scattered beam would no longer be proportional to the velocity of coagulation. As, however, the results obtained with the Tyndallmeter are in general agreement with those obtained with the microphotometer, it is clear that the divergences from Smoluchowski's theory as obtained in the present experiments are real and are not due to any shortcomings of the experimental arrangements used.

It thus seems reasonable to conclude that all explanations based on such factors as deviations from monodispersity, presence of traces of electrolytes, etc., are inadequate to account for the divergences from Smoluchowski's theory in the region of slow coagulation.

The principal difference between slow and rapid coagulation is that in the former case the particles are only partially discharged whilst in the latter case they are nearly completely so. In the case of slow coagulation this residual electric charge on the particles is thus too important a factor to be neglected and accordingly an attempt has been made to study the problem from this point of view. The results are given in the next part of this paper.

The author wishes to express his best thanks to Dr. G. B. Banerji for the microphotometer prints and to Dr. P. B. Ganguly for the kind interest during the progress of this work.

## The Kinetics of Slow Coagulation. Part II.

By D. N. GHOSH.

Numerous attempts have been made from time to time to experimentally verify Smoluchowski's theory. Thus Westgren and Reitstötter (*Z. physikal. Chem.*, 1918, **92**, 750), working with coarse gold sol and Kruyt and van Arkel (*Rec. Trav. Chim.*, 1920, **39**, 654), in the case of selenium sols have shown that Smoluchowski's theory is capable of experimental verification in the region of rapid coagulation of colloids. When, however, attempts were made to verify Smoluchowski's theory with respect to slow coagulation, the agreement with experimental data was not satisfactory. Thus Kruyt and van Arkel (*Kolloid Z.*, 1923, **32**, 29), Mukherjee and Papacostantinou (*J. Chem. Soc.*, 1920, 117, 1563), Mukherjee and Mazumdar (*ibid.*, 1924, 125, 785), Desai (*Trans. Faraday Soc.*, 1928, **24**, 181), Mehta and Miss Joseph (*J. Indian Chem. Soc.*, 1933, **10**, 182), working with different sols have all found more or less marked divergences from the theory.

Smoluchowski has accounted for the difference between slow and rapid coagulation by introducing a factor  $\epsilon$  in his equation for rapid

coagulation, 
$$V_1 = \frac{V_0}{1 + \epsilon \frac{t}{T}},$$

where  $\epsilon$  is unity in the case of rapid coagulation and has a value less than unity in the case of slow coagulation. This would mean that in the case of rapid coagulation all the collisions between completely discharged particles end in adherence, while in the case of slow coagulation only a fraction of them are so, owing to the residual charges possessed by the particles. He further assumes that in the latter case the fraction  $\epsilon$  remains a constant during the course of each coagulation, which demands that all the different coagulation curves should be "affine" to one another. But an examination of the series of coagulation curves shows that this is far from the case. This fact together with the general autocatalytic nature of these curves which cannot find a place

in Smoluchowski's theory, goes definitely to show that the rates of slow coagulation are being influenced by some additional factor, which vanishes when the particles are completely discharged.

Now of the two factors, (i) the probability of collision and, (ii) the probability of adherence, which determine coagulation, it is only the latter that is affected by the residual charge of the partially discharged particles (*cf.* Kruyt, A. Smith, "Colloid Chemistry" Vol. I, p. 307). It was hoped, therefore, that a consideration of the electrical energy possessed by the particles as they grow, might throw some light on the behaviour of the adherence factor during slow coagulation.

It has been shown by Burton (*Phil. Mag.*, 1906, 12, 472), that a colloid particle with its double layer can be considered as a charged condenser, having an energy  $E$ , given by the equation  $E = Q^2/2C$ , where  $Q$  is the charge and  $C$  is the capacity of the condenser. Further, if we assume (*cf.* Smoluchowski)  $P_2, P_3, P_4$ , the double, triple and quadruple particles formed from the single particles  $P_1$  as spherical, then their radii  $r_2, r_3, r_4$ , etc., and capacities  $C_2, C_3, C_4$ , etc., can easily be expressed in terms of  $r_1$  and  $C_1$ , the radius and capacity of the primary particle. Thus,

$$r_2 = r_1 \sqrt[3]{2} = 1.26 r_1$$

$$r_3 = 1.44 r_1$$

$$r_4 = 1.59 r_1$$

$$r_5 = 1.71 r_1$$

Similarly the capacities (assuming  $d$ , the thickness of the double layer for the primary particles to be the same as for the multiple particles) are as follows:

$$C_1 = \frac{r_1^2}{d}$$

$$C_2 = \frac{r_2^2}{d} = \frac{(1.26r_1)^2}{d} = 1.59C_1$$

$$C_3 = \frac{r_3^2}{d} = 2.07C_1$$



$$C_4 = \frac{r_4^2}{d} = 2.53C_1$$

$$C_5 = \frac{r_5^2}{d} = 2.92C_1.$$

Now, if two charged condensers are joined together it can be proved that there is always a loss of electrical energy except when the initial potentials are the same. Thus, if  $Q_1$ ,  $C_1$  and  $V_1$ , and  $Q_2$ ,  $C_2$ , and  $V_2$  be the charges, capacities and potentials of two charged condensers, then the total energy before connecting is given by the equation,

$$E_1 = \frac{1}{2} \cdot \frac{Q_1^2}{C_1} + \frac{1}{2} \cdot \frac{Q_2^2}{C_2}.$$

After connecting we have,

$$E_2 = \frac{(Q_1 + Q_2)^2}{2(C_1 + C_2)}$$

whence the loss of energy,

$$\begin{aligned} E_1 - E_2 &= \frac{1}{2} \left\{ \frac{Q_1^2}{C_1} + \frac{Q_2^2}{C_2} - \frac{(Q_1 + Q_2)^2}{(C_1 + C_2)} \right\} \\ &= \frac{1}{2} \cdot \frac{(Q_1 C_2 - Q_2 C_1)^2}{C_1 C_2 (C_1 + C_2)}. \end{aligned}$$

This is equal to zero, only when  $Q_1 C_2 = Q_2 C_1$

or when  $\frac{Q_1}{C_1} = \frac{Q_2}{C_2}$ , i.e., when  $V_1 = V_2$ .

If then we assume that the charges  $q_2, q_3, q_4$ , etc. of particles  $P_2, P_3, P_4$ , etc., are equal to  $2q_1, 3q_1, 4q_1$ , etc., respectively.  $q_1$  being the charge of the primary  $P_1$ , it will be possible to compute the energy losses from equation (1) for the different cases corresponding to combination between differently sized particles as in the following:

*Case 1.* Combination between  $P_1$  and  $P_1$ .

Energy lost = 0, since the two particles are initially at the same potential.

**Case 2.** Combination between  $P_1$  and  $P_2$ .

$$\begin{aligned}\text{Energy lost} &= \frac{1}{2} \cdot \frac{(1.59 C_1 q_1 - 2 q_1 C_1)^2}{C_1 \times 1.59 C_1 \times 2.59 C_1} \\ &= \frac{1}{2} \cdot \frac{q_1^2}{C_1} \times 0.07 = 0.07 E_1. \quad [\because E_1 = \frac{q_1^2}{2 C_1}]\end{aligned}$$

**Case 3.** Combination between  $P_1$  and  $P_3$ .

$$\begin{aligned}\text{Energy lost} &= \frac{1}{2} \cdot \frac{(2.07 C_1 q_1 - 3 q_1 C_1)^2}{C_1 \times 2.07 C_1 \times 3.07 C_1} \\ &= 0.14 \times \frac{q_1^2}{2 C_1} = 0.14 E_1.\end{aligned}$$

**Case 4.** Combination between  $P_1$  and  $P_4$ .

$$\begin{aligned}\text{Energy lost} &= \frac{1}{2} \cdot \frac{(2.53 C_1 q_1 - 4 q_1 C_1)^2}{C_1 \times 2.53 C_1 \times 3.53 C_1} \\ &= 0.24 \times \frac{q_1^2}{2 C_1} = 0.24 E_1.\end{aligned}$$

**Case 5.** Combination between  $P_1$  and  $P_5$ .

$$\text{Energy lost} = \frac{1}{2} \cdot \frac{(2.92 C_1 q_1 - 5 q_1 C_1)^2}{C_1 \times 2.92 C_1 \times 3.92 C_1} = 0.38 E_1.$$

**Case 6.** Combination between  $P_2$  and  $P_2$ .

Energy lost = 0, since both are at the same potential.

**Case 7.** Combination between  $P_2$  and  $P_3$ .

$$\begin{aligned}\text{Energy lost} &= \frac{1}{2} \cdot \frac{(2.07 C_1 \times 2 q_1 - 3 q_1 \times 1.59 C_1)^2}{1.59 C_1 \times 2.07 C_1 \times 3.66 C_1} \\ &= 0.03 \times \frac{q_1^2}{2 C_1} = 0.03 E_1\end{aligned}$$

It will appear from the above calculations that the amounts of energy lost in the cases 1—7 are in the ration of 0: 1: 2: 3.6: 3.8: 0: 0.03.

5.5: 0:0.5 which shows that the more complex the particles with which a primary particle combines, the greater is the loss of energy.

If we assume with Burton (*loc. cit.*) that a colloid particle with its double layer can be considered as a charged condenser we can apply the above considerations in considering the distribution of charges with the growth of the particles. It has been shown by Rene Audubert (*Ann. Physik*, 1922, 18, 5; Alexander "Colloid Chemistry," Vol I, p. 360) that the particles in a sulphur sol are nearly spherical in form and "the aggregation conserves the spherical form of the grains" Thus in the case of the sulphur sol studied here the distribution of the charge on the surface of the primary as well as of the complex particles remains uniform as in the case of metallic spherical condensers. Now, any unstable system when left to itself will tend towards a state with minimum energy content. In other words, it will follow that course, in which there is maximum loss of energy. If then we regard a monodisperse sol—electrolyte mixture coagulating slowly as such a system and associate the rate of coagulation with the rate of loss of energy, it is apparent from the above considerations, that during the earlier stages there will be little tendency towards coagulation since as in case 1, the combination between two single particles to give a double one entails no loss of energy. From the cases considered above it is apparent that in the case of a combination of a primary particle with a multiple particle there is a greater loss of electrical energy than in the case of combination between two primary particles. This loss increases with the increase in the complexity of the multiple particle. Thus with the advance of coagulation the probability is that the  $P_1$  particles will combine more and more with particles of gradually increasing complexity. This conclusion is supported by the ultra-microscopic observations of Wiegner (*Koll. Chem. Beih.*, 1916, 8, 65, and of Galecki (*Z. anorg. Chem.*, 1912, 74, 174) who observed that during the process of slow coagulation instead of two primary particles combining with each other, the primary particles combined preferably with multiple particles.

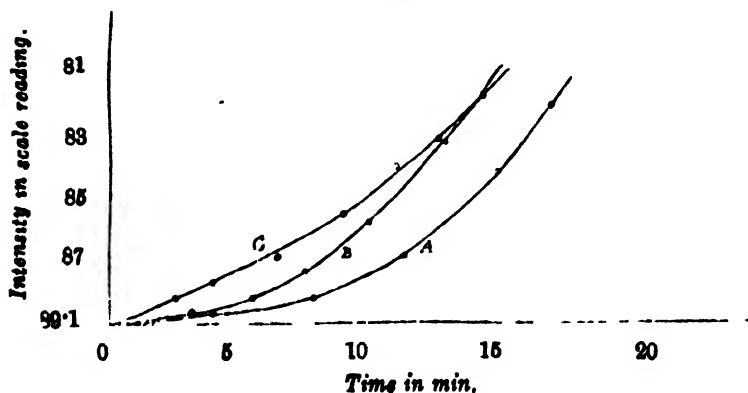
In slow coagulation, therefore, with partially discharged particles the rate at any stage will depend on (a) the number of primary particles, and, (b) the number of multiple particles.

The S-shaped autocatalytic nature of slow coagulation curves observed by so many different investigators, can now be easily explained. Initially (a) is high and (b) is low, whence the rate is slow

as in the lower part of the S-shaped curves. As  $(b)'$  is increasing and  $(a)$  is decreasing, a time soon comes when both  $(a)$  and  $(b)$  have considerably high values. It is here that the rate is very high as in the steep portion of the S-shaped curves. After this stage is passed there is a great diminution of  $(a)$  and though  $(b)$  is high, the rate is slowed down again as in the top portion of the S-shaped curves. Thus it is the dearth of the multiple particles in the beginning and the dearth of the primary particles towards the end which are responsible for the slowness of the rate in the beginning and in the end.

Attempts have been made to verify the above conclusions by diluting the sol and by inoculating the system with coarse particles. When a sol is fairly diluted the autocatalytic nature of the coagulation process vanishes as can be seen clearly from Fig. 2 in Part I (p. 510). Desai and Patel (*Trans. Faraday Soc.*, 1930, 26, 128) have also found that the coagulation of  $\text{ThO}_2$  sol loses its autocatalytic nature on dilution. According to the considerations advanced here, the effect of dilution is to decrease the concentration of primary particles in the system. For the rate of coagulation to increase, it is necessary that the concentration of both primary and complex particles must be high. In the case of the dilute sol the concentration of primary particles is fairly low from the beginning and hence the proportion between the concentration of primary and secondary particles always remains lower than that in the case of a concentrated sol. Consequently there is no abrupt rise in the rate of the reaction and the autocatalytic nature is much less prominent than that in the case of a concentrated sol.

FIG. 1.



In a series of experiments, 0.5 c.c. of sulphur sol was mixed with 1.5 c.c. of  $N/4$ -KCl and 3 c.c. of water and the rate of coagulation was followed on the Tyndallmeter. The results are plotted in curve A of Fig. 1, which is distinctly autocatalytic. The experiments were repeated with sols which were inoculated with some coarse particles. The inoculation was done by adding to a fresh sample of the sol-electrolyte mixture, a few drops of the same mixture where coagulation has been allowed to proceed for a period of 10 and 14 minutes. The results are shown in the curves B and C of Fig. 1, whence it will be seen that the autocatalytic nature becomes less pronounced in curve B and practically vanished in curve C. Thus when a sol is inoculated with sufficient coarse particles its coagulation is no longer autocatalytic. This behaviour is readily explained on the basis of the considerations advanced in the earlier parts of this paper. The inoculation of a sol with coarse particles really means an increased concentration of complex particles in the system. Thus from the very beginning there is an appreciable concentration of both primary and multiple particles. Hence the chances of adhesion are fairly large all throughout and the slow rate of coagulation usually observed in the initial stages is no longer prominent.

It has been shown in Part I (*loc. cit.*) that the deviation from Smoluchowski's equation in the slow coagulation of a monodisperse sulphur sol is such that the rate is higher than that required by the theory. On the other hand with a polydisperse  $As_2S_3$  sol, Mukherjee and Papaconstantinou (*loc. cit.*) have shown that the rate becomes slower and slower than that required by the theory. Anderson (*Trans. Faraday Soc.*, 1923, 19, 623) has tried to explain this slowness by assuming that the particles are initially possessed of different amounts of charges, so that as coagulation proceeds those with smaller charges are soon coagulated leaving behind the others with higher charges as a result of which the rate becomes slower and slower. This explanation, however, does not satisfy the observation on the monodisperse sulphur sol, where an increase has been obtained.

From the considerations advanced above it is clear that in a monodisperse sulphur sol coagulating slowly, the accelerating effect due to the gradual appearance of complex particles in the system will be more prominent. However, in the case of a polydisperse  $As_2S_3$  sol this effect will be marked by the retarding effect due to the fast disappearance of the primary particles which readily combine with

the complex particles already present, so that only the latter having less tendency to combine between themselves are left behind.

In a polydisperse sol, therefore, the autocatalytic nature of the coagulation curves will be less pronounced than in a monodisperse sol. This is actually the case as has been shown by the author (*J. Indian Chem. Soc.*, 1932, 9, 591) with an  $\text{As}_2\text{S}_3$  sol, where the S shaped curve appears only at one or two particular electrolyte concentrations, whereas with the monodisperse sulphur sol, unless very dilute, the autocatalytic nature persists over a wider range of electrolyte concentrations (*cf.* Fig. 1, Part I).

If now the deviations from Smoluchowski's equation during the later stages of slow coagulation be really due to the appearance of these complex particles, then this disturbing effect can be minimised to a great extent, if not altogether avoided, by inoculating the sol initially with some coarse particles as mentioned above. Accordingly a set of measurements were first taken without any inoculation and the results are given in Table I.

TABLE I.

Curve →	I.	II.	III.	IV.	V.	VI.					
Electrolyte conc. (m. mols./litre) →	125	100	85	80	75	70	Ratio values.				
Intensity (scale readings).	$T$ (sec)	$T_1$	$T_2$	$T_3$	$T_4$	$T_5$	$\frac{T_1}{T}$	$\frac{T_2}{T}$	$\frac{T_3}{T}$	$\frac{T_4}{T}$	$\frac{T_5}{T}$
88.5	9	45	192	198	480	615	5	21	22	53	68
88	12	70	222	300	570	810	5.8	18	25	47	67
87	16	92	267	402	690	1050	6	19	25	43	65
86	21	108	312	460	790	1260	5	15	21	38	60
85	27	126	350	510	870	1425	5	13	19	31	52
84	32	140	390	560	942	1620	4.5	12	17	29	51
83	36	156	420	606	1020	1710	4	11	16	28	48

From these data, a series of curves I—VI, have been obtained, whence it is seen that to reach the same stage of coalescence, say, corresponding to I value 85.5, the times taken are, 24 seconds 2, 5½, 8, 14, and 22½ minutes respectively, for the different rates

of coagulations as represented in curves I—VI. If now, the above measurements are repeated, with inoculation with a fixed small quantity of the corresponding sol—electrolyte mixtures, the particles on which have been allowed to grow for the above periods, then the curves so obtained should be in a sense comparable between themselves, since the only effect of thus inoculating, is to introduce the same number of similar coarse particles every time without changing the electrolyte concentration. Thus corresponding to curve II in Fig. 2, a mixture of 2 c.c. of  $N/4$ -KCl and 0.5 c.c. of sulphur sol with 2.5 c.c. of water was allowed to grow for 2 minutes at the end of which 0.5 c.c. of this semi-turbid mixture,  $\frac{1}{2}$  c.c. of  $N/4$ -KCl, 0.5 c.c. of sulphur sol and 2.5 c.c. of water were mixed together simultaneously and the rate of coagulation was followed by the Tyndallmeter as represented in curve II (a), Fig. 3. In the same way curves I (a) to VI (a) were obtained as plotted in Fig. 3 from the data given in Table II.

FIG. 2.

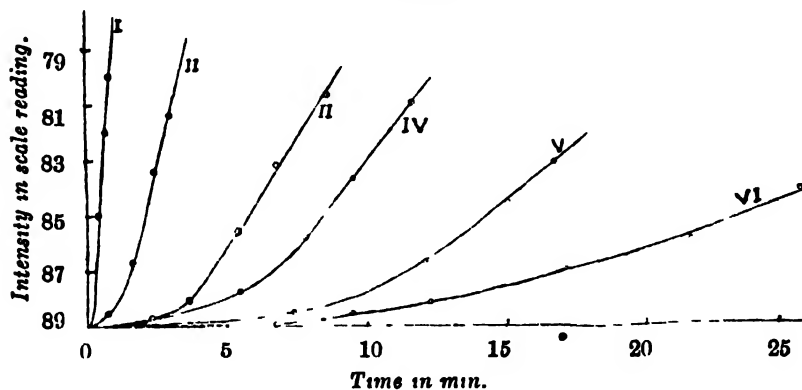


FIG. 3.

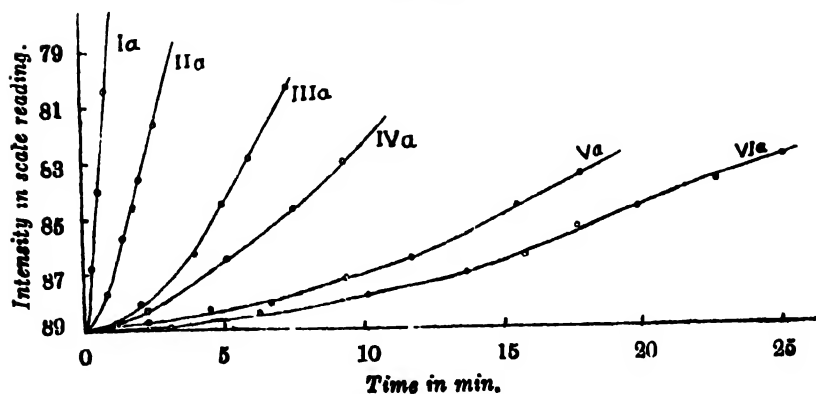


TABLE II.

Curve →	I.	II.	III.	IV.	V.	VI.						
Electrolyte conc. (m. mols./litre) →	125	100	85	80	75	70						
Intensity (scale reading).							Ratio values.					
	$T$ (Sec).	$T_1$	$T_2$	$T_3$	$T_4$	$T_5$	$\frac{T_1}{T}$	$\frac{T_2}{T}$	$\frac{T_3}{T}$	$\frac{T_4}{T}$	$\frac{T_5}{T}$	
88.5	9	27	102	120	240	375	3	11	13	27	41	
88	12	42	144	174	402	570	3.5	12	14	33	47	
87	16	63	200	260	615	840	4	12	16	37	52	
86	21	80	240	348	774	1002	4	11	16	32	49	
85	27	96	278	420	897	1152	4	10	15	33	43	
84	32	110	312	495	1020	1305	3.5	10	15	32	44	
83	36	126	348	555	1100	1488	3.5	10	15	31	41	

A comparison of the values of the constants  $T_1/T$ ,  $T_2/T$ , etc., from Tables I and II at once shows that whereas in the former it is steadily decreasing, it is fairly constant in the latter, which supports the views advanced before.

The above considerations throw a greater insight into the mechanism of slow coagulation in as much as coagulation takes place more by the growth of the primary particles on the multiple particles present in the sol than by forming fresh combinations between primary particles themselves. This also satisfactorily explains a number of well known phenomena in Colloid Chemistry. Thus, the disappearance of autocatalytic nature on continued dialysis of the sol, as observed by Desai and Patel (*loc. cit.*) on  $\text{ThO}_2$  sol can be attributed to the continued increase in the number of complex particles formed in the sol owing to the gradual removal of the peptising ions which also explains the continuous decrease in the flocculation value of KCl with the progress of dialysis of a  $\text{e}(\text{OH})_3$  sol as observed by Desai and Barve (*Nature*, 1981, 128,



907).\* The phenomena of "acclimatisation" and "ageing effect" may also be similarly attributed to the difference in the number of complex particles formed in the same sol under different conditions.

It thus seems reasonable to conclude that Smoluchowski's theory is of limited applicability to cases of slow coagulation,  $\epsilon$ , the "adherence factor" is not a constant but a function of time, increasing with it along with the growing size of the particles.

The author wishes to thank Dr. P. B. Ganguly for his kind interest in this work.

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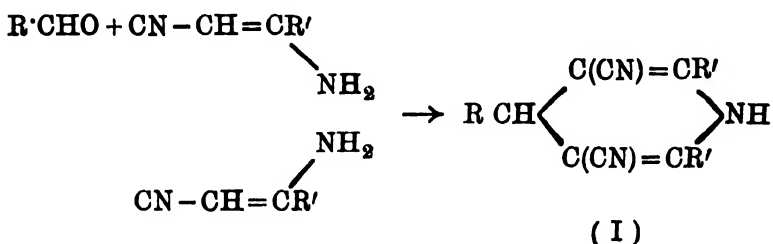
\* The recent observation by Mehta and Joseph (*loc. cit.*) that the rate of coagulation of an imperfectly dialysed  $\text{TiO}_2$  sol is higher, while that of the same sol with prolonged dialysis is lower than that required by Smoluchowski's theory, also receives a similar interpretation.



## Reactions of Dinitriles with Aromatic Hydroxyaldehydes.

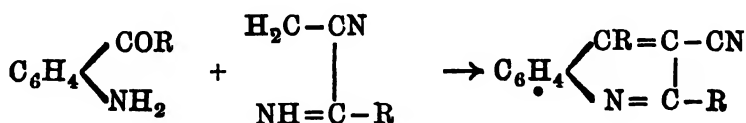
BY NIRMALANANDA PALIT.

Simple aliphatic and aromatic aldehydes have been found to react with the bimolecular nitriles (imidoacetylmethylcyanides) to form substituted 3:5-dicyanodihydropyridine derivatives (Meyer, *J. pr. Chem.*, 1908, 78, 507 ; Mohr, *ibid.*, 1897, 56, 124).

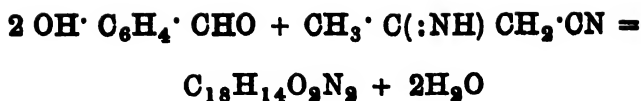


(R = H, Me, Ph, anisyl, piperonyl, cinnamyl etc., R' = Me, Ph.)

In the present investigation aromatic hydroxyaldehydes have been employed to see if the presence of the additional hydroxyl group modifies the above general course. It was expected that with the *o*-hydroxyaldehyde (salicylaldehyde) the dinitrile would react in the tau tomeric imino form to give 3-cyanoquinoline derivatives in the same way as *o*-aminobenzaldehyde and *o*-aminoacetophenone react with it (Myer, *ibid.*, 1914, ii, 90, 1).



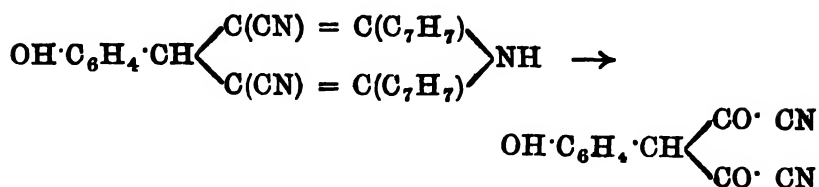
It was found, however, that the reaction did not proceed in this direction at all but followed an entirely different course. Mohr (*loc. cit.*) who used diacetonitrile only, found that curiously enough two molecules of the aldehyde reacted with one molecule of the dinitrile with the elimination of two molecules of water and he could not decide the constitution of the product.



On extending the reaction to the case of other dinitriles, it has been found by the author that the above is the general course of reaction with salicylaldehyde, although by modifying the conditions of experiment a dicyanodihydropyridine derivative (I) could be obtained only from *p*-toluacetodinitrile. In order to elucidate the constitution of Mohr's class of compounds, the following evidence has now been brought forward to indicate the presence of a xanthhydryl ring in it.

The absence of a phenolic hydroxyl group, aldehyde, imido or amido group is shown by the facts that it is not soluble in alkali, does not reduce Schiff's reagent, nor is oxidised to an acid by permanganate solution and it is insoluble and unchanged in boiling hydrochloric acid. It may contain a cyanogen group since it easily goes into solution in strong sulphuric acid in the cold. No carboxylic acid has yet been obtained from the solution. It is interesting to note that although it contains no hydroxyl (phenolic) or amido group, it gives a monoacetyl derivative with greatest ease in the cold. No polyacetyl derivative could be obtained even on boiling. This indicates the presence of an alcoholic hydroxyl group. When heated with fuming hydrochloric acid in a sealed tube it takes up a molecule of water and the product is a phenol soluble in alkali, indicating thereby the presence of an oxygen atom in the ring which undergoes fission during hydrolysis. Attempt was made to prepare the triacetyl derivative of the hydrolysis product, but a mixture of polyacetyl derivatives was obtained which could not be separated. To avoid the production of this mixture, the substance was first methylated and subsequently acetylated but yet no pure compound could be obtained. The above evidence suggests the presence of a xanthhydryl ring in it, although like xanthhydryl it is neither easily oxidised nor combines energetically with urea in alcoholic solution.

While salicylaldehyde behaved in the above abnormal way, *m*- and *p*-hydroxybenzaldehydes condensed with the dinitriles in the usual manner and the best conditions for condensation have been studied. In attempting to oxidise the dihydropyridines so obtained by nitrous acid gas, the expected pyridine was not formed in the case of *m*-hydroxybenzaldehyde and an analysis showed that the molecule was ruptured to yield a ketone thus,



No semicarbazone or phenylhydrazone of this ketone could be obtained due to the insoluble nature of the substance, but its formation received confirmation from the fact that the same compound was also produced when the corresponding dihydropyridine from benzoacetodinitrile was similarly oxidised. Such oxidation proceeded much more smoothly when glacial acetic acid was used as the medium in place of absolute alcohol. With the dihydropyridines from *p*-hydroxybenzaldehyde, the oxidation proceeded in the normal way to yield pyridines, but they are not basic and are insoluble in acids, due probably to the cyanogen groups.

#### EXPERIMENTAL.

Three dinitriles were prepared by condensing methylcyanide with phenylcyanide, *p*-tolucyanide and *p*-methoxyphenylcyanide. The first two have been previously obtained, but it has now been found that the yields are much improved when the mixture of the nitriles is heated with molecular sodium in ether for 9 hours and then allowed to stand overnight.

*p*-Anisylacetodinitrile.—Molecular sodium (13·8 g.) was suspended in dry ether containing anisylcyanide (40 g.). Methylcyanide (24·5 g.) was added in drops at ordinary temperature. After half the quantity was added, the mixture was warmed on the water-bath, when brisk action ensued. The mixture was finally heated on the water-bath for 9 hours and allowed to stand overnight. The cream coloured sodium derivative was filtered, washed with dry ether thoroughly, and when dry, was gradually added to cracked ice. It was washed, dried and crystallised from alcohol, m. p. 117°, yield 80 g; 7 g. of unchanged anisylcyanide were recovered from the ether washings. (Found: C, 69·04; H, 5·89; N, 16·28.  $\text{C}_{10}\text{H}_{10}\text{ON}_2$  requires C, 68·96; H, 5·74; N, 16·09 per cent).

#### Condensation with Salicylaldehyde.

*p*-Toluacetodinitrile.—A mixture of the dinitrile (5·2 g.) and the aldehyde (8·6 g.) was heated in boiling water for 9 hours; strong

smell of ammonia was perceived and the liquid set to a hard solid on cooling. It was washed with caustic soda and water, dried and subsequently digested with boiling acetone when a white powder was left behind (yield 8 g.). It is insoluble in alcohol and petroleum ether, dissolves with difficulty in acetone and ethyl acetate, more easily soluble in benzene from which it is crystallised, m. p. 217-18°. (Found: C, 78.77; H, 5.00; N, 7.63.  $C_{24}H_{18}O_3N_2$  requires C, 78.68; H, 4.91; N, 7.65 per cent).

The *acetyl* derivative.—The substance quickly went into solution in excess of acetic anhydride and a drop of concentrated  $H_2SO_4$  and after 5 minutes the solution was poured into water and the product collected and crystallised from acetic acid, m. p. 180-81°. (Found: C, 76.43; H, 4.89; N, 6.97.  $C_{26}H_{20}O_3N_2$  requires C, 76.47; H, 4.90; N, 6.86 per cent). The same monoacetyl derivative was also produced when the substance was boiled under reflux with excess of acetic anhydride and a drop of pyridine.

*Hydrolysis*.—The substance was heated in a sealed tube with concentrated HCl at 180-85° for 4 hours (at 150-55° the substance is recovered unchanged), when a deep red glass-like globule stuck to the sides of the tube. It is insoluble in sodium carbonate but dissolves in caustic soda with a beautiful violet colour and is reprecipitated on acidification. It was crystallised from alcohol as a vermilion powder, m.p. 198° (shrinking). (Found: C, 74.98; H, 5.32; N, 7.49.  $C_{24}H_{20}O_3N_2$  requires C, 75.00; H, 5.20; N, 7.29 per cent).

The *methoxy* derivative was prepared in the usual way with dimethylsulphate. The resulting yellow mass subsequently solidified and after preliminary purification from methyl alcohol melts at 100-10°. It could not be crystallised for analysis.

*p-Toluacetodinitrile in glacial acetic acid*.—The aldehyde and the dinitrile were dissolved in the acid and heated on the water-bath for 2 hours, when solids began to separate immediately on warming. This is probably the open-chain diamine representing the intermediate compound in (I). It gradually went into solution and a crystalline deposit was formed on cooling. It was twice crystallised from acetone or a large volume of acetic acid, m. p. 266-67° with a little previous shrinking. It dissolves in hot caustic soda and is reprecipitated on acidification. (Found: C, 80.43; H, 5.54; N, 10.25.  $C_{27}H_{21}ON_3$  (Type I) requires C, 80.39; H, 5.21; N, 10.42 per cent).

*Benzoacetodinitrile*.—When the mixture of salicyl-aldehyde and benzoacetodinitrile was heated on the water-bath for 9

hours and subsequently washed with acetone, a white powder was left behind which was twice crystallised from benzene, m. p. 225-26°. (Found: N, 8.12.  $C_{23}H_{16}O_2N_2$  requires N, 7.95 per cent).

The same product was obtained even when the condensation was attempted in acetic acid. Having failed to obtain the dihydropyridine derivative in this way the condensation was next tried in acetic acid in presence of dry HCl gas. The liquid was worked up after a week and the product crystallised from acetic acid in wooly needles, m. p. 291-92°. (Found: C, 78.56; H, 4.82; N, 8.22.  $C_{23}H_{16}O_2N_2$  requires C, 78.40; H, 4.54; N, 7.95 per cent). This substance has the same empirical formula as Mohr's class of compounds. To determine if this peculiar influence of HCl gas as condensing agent is general, the condensation was attempted with *p*-toluacetodinitrile also. The product crystallised from pyridine in shining silky mass melting above 300° but again having the same percentage composition as Mohr's class of compounds.

*Anisylacetodinitrile*.—The condensation was effected with or without acetic acid, but the same product was produced. It crystallised from benzene, m. p. 247-48°. (Found: N, 7.64.  $C_{24}H_{18}O_3N_2$  requires N, 7.33 per cent).

#### *Condensation with p-Hydroxybenzaldehyde.*

*Benzoacetodinitrile*.—The acetic acid solution was boiled for 1½ hours; copious light crystals were collected overnight.\* The product was twice crystallised from acetic acid, m. p. 218-19°. (Found: C, 80.12; H, 4.68; N, 11.28.  $C_{25}H_{17}ON_3$  (Type I) requires C, 80.00; H, 4.53; N, 11.20 per cent).

The oxidation of the above compound was carried out by passing nitrogen trioxide into an alcoholic suspension cooled in ice for 3 hours. The mixture was kept in ice overnight and the light bulky mass, which dissolves freely in acetone, crystallised three times from absolute alcohol; it shrinks at 255° and melts at 265°. (Found: C, 80.52; H, 4.24; N, 11.48.  $C_{25}H_{15}ON_3$  requires C, 80.42; H, 4.02; N, 11.26 per cent).

\* In all these condensations with *m* and *p*-hydroxyaldehydes, there is a time limit for heating the mixture, for too much boiling always results in a side reaction where the solid that first separates goes into solution to yield a gummy impure mass.

*p-Toluoacetodinitrile*.—The solution in acetic acid on boiling for 7 minutes deposited pale yellow sandy crystals and the reaction was complete in  $\frac{1}{2}$  hour. It is insoluble in benzene, ligroin, soluble with difficulty in acetic acid, easily in acetone, pyridine and caustic soda. It was crystallised from acetic acid, m.p. 259-60°. (Found: C, 80.41; H, 5.86; N, 10.50.  $C_{27}H_{21}ON_3$  requires C, 80.39; H, 5.21; N, 10.42 per cent).

On oxidation it gave a white gelatinous cake which on drying, assumed a deep orange brown colour on exposure. It was repeatedly crystallised from acetone till it no longer changed colour on exposure, m.p. 245-46°. (Found: C, 80.88; H, 4.91; N, 10.75.  $C_{27}H_{19}ON_3$  requires C, 80.80; H, 4.74; N, 10.47 per cent).

*Anisylacetodinitrile*.—The condensation was carried as usual, and a solid separated immediately on warming, which was filtered after an hour without allowing to cool. When crystallised from acetone it softens at 379° and melts at 385°. (Found: C, 74.63; H, 5.00; N, 9.58.  $C_{27}H_{21}O_3N_3$  requires C, 74.48; H, 4.82; N, 9.65 per cent).

On oxidation a flocculent light precipitate appeared quickly. It was kept in an ice chest for a day and filtered. A bulky milk white substance was obtained which shrank enormously on drying and assumed a deep yellow colour on exposure. Light white feathery crystals melting at 248-50° separated from acetone. (Found: C, 74.98; H, 4.58; N, 9.85.  $C_{27}H_{19}O_3N_3$  requires C, 74.82; H, 4.38; N, 9.70 per cent).

#### *Condensation with m-Hydroxybenzaldehyde.*

*Anisylacetodinitrile*.—On boiling the solution in acetic acid clusters of needles began to separate within 10 minutes. The colour darkened to deep red and the reaction was complete in  $1\frac{1}{2}$  hours. The liquid crystallised *en masse* overnight. It was twice crystallised from acetic acid, m.p. 218-20°. (Found: N, 9.78.  $C_{27}H_{21}O_3N_3$  requires N, 9.65 per cent).

Repeated attempts to oxidise it in the usual way resulted in complex mixtures which on careful purification always gave substances with much higher nitrogen content. The substance was dissolved in warm acetic acid, cooled and saturated with  $N_2O_3$ . Next day the unchanged crystals were redissolved by warming and the flask was heated on the water-bath. The brown fumes were gradually used up and the solid no longer crystallised on cooling showing



that the reaction was complete. The deep yellow liquid was evaporated to dryness and the solid crystallised from acetone, m.p. 256-57°. It dissolves in cold alkali. [Found: C, 61·68; H, 2·95; N, 13·32.  $C_{11}H_6O_3N_2$  (ketone) requires C, 61·68; H, 2·80; N, 13·08 per cent].

*Toluacetodinitrile*.—The condensation was effected as usual and the product crystallised from acetic acid, m.p. 269-70°. It turns beautiful violet on exposure. (Found: N, 10·44.  $C_{27}H_{21}ON_3$  requires N, 10·42 per cent).

The oxidation gave a light bulky mass which crystallised from acetone in silky fibres resembling those from anisylacetodinitrile by oxidation. It has the same m.p. 256-57° which is unaltered when the two substances are mixed. On analysis it showed the same composition.

*Benzoacetodinitrile*.—The condensation product was twice crystallised from acetic acid, m. p. 267-68°. (Found: N, 11·36.  $C_{25}H_{17}ON_3$  requires N, 11·20 per cent).

In conclusion, I wish to thank Prof. A. S. Khan for giving me facilities to carry out this work in this laboratory. My best thanks are also due to Dr. P. C. Mitter and Dr. J. C. Bardhan of the University College of Science, Calcutta, for their kind interest and material help with some chemicals.

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# On the Ethyl and Methyl Esters of Fluocarbonic Acid.

By HARISH CHANDRA GOSWAMI AND PULIN BIHARI SARKAR.

Search for the literature shows that free halogenocarbonic acids have not been isolated, only the ethyl and methyl esters of chlorocarbonic acid being known.

Moissan (*Bull. Soc. chim.*, 1891, iii, 5, 456) introduced silver fluoride as the fluorinating agent. Meslans (*compt. rend.*, 1892, 114, 1020) obtained acetyl fluoride by the action of anhydrous zinc fluoride on acetyl chloride. Swarts (*Bull. Soc. chim. Belg.*, 1930, 89, 444)\* introduced  $\text{SbF}_3$  and a small quantity of  $\text{SbCl}_5$  or bromine (as catalyst) as well as  $\text{Hg}_2\text{F}_2$  as fluorinating agents. The affinity of fluorine for carbon is enormous which is demonstrated by the remarkable stability of the covalent linkages of these two atoms. Fluocarbonic esters are, therefore, expected to be quite stable. Attempts to prepare the fluocarbonic esters from the corresponding chlorocarbonic esters with any of the above methods were unsuccessful, explosive decomposition with the evolution of alkyl fluoride taking place.

On the other hand, by the action of anhydrous thallous fluoride on the ethyl and methyl esters of chlorocarbonic acid we have been able to isolate the corresponding fluocarbonic esters. They are pungent smelling liquids lachrymatory, boiling respectively at  $57^\circ$  (ethyl ester) and  $40^\circ$  (methyl ester). In the absence of moisture they do not attack glass.

The substitution of chlorine by fluorine lowers the boiling point by  $86^\circ$  and  $32^\circ$  in case of ethyl and methyl esters. The methyl ester is found to be denser than the ethyl ester, the same being the case with the initial chlorocarbonic esters. It is interesting to compare the boiling points of the acid chlorides and acid fluorides previously described in the literature.

		B.p.	Difference.
Methyl chlorocarbonate	$d_{15}, 1.236$	$71.4^\circ$	
Methyl fluocarbonate	$d_{33}, 1.06$	$40^\circ$	81.4
Ethyl chlorocarbonate	$d_{15}, 1.144$	$93^\circ$	
Ethyl fluocarbonate	$d_{33}, 1.11$	$57^\circ$	86
Acetyl chloride		$52^\circ$ (720 mm.)	
Acetyl fluoride		$20.8^\circ$ (770 mm.)	31.2
Propionyl chloride		$80^\circ$	
Propionyl fluoride		$44^\circ$	36

\* Communication to the Science Congress in Bruxelles in July, 1930.

## EXPERIMENTAL.

*Method of Analysis.*

*Estimation of C and H.*—The ordinary method of analysis of organic compounds is to be modified for the following reasons: (1) Organic fluocccpounds heated in contact with glass yield  $\text{SiF}_4$  which is not decomposed by  $\text{CuO}$  maintained at a dull red heat. (2) Hydrofluoric acid vapour is incompletely decomposed by  $\text{CuO}$ .

The analysis was carried out as recommended by Moissan (*Ann. chim. Phys.*, 1890, vi, 19, 277) ; the combustion was effected in a current of oxygen in a metal tube by means of a mixture of  $\text{CuO}$  (80%) and litharge (20%), the latter retaining all fluorine as oxyfluoride. The metal tube used in this case was a copper tube filled with the aforesaid mixture and heated to redness in an electric furnace. In order to prevent the two end corks from charring a lead tube, through which cold water was circulated, was coiled round the ends. The substance to be analysed was weighed in a capillary tube introduced into hard glass tube drawn to a capillary end and placed close to the end of the copper tube. It was then cautiously vapourised in a slow current of dry oxygen by means of a regulated tiny microburner.

*Estimation of fluorine.*—Generally the fluorine directly linked to carbon is extremely difficult to analyse. In these cases no such difficulty was experienced owing to the presence of a doubly linked oxygen attached to the same carbon atom.

The sealed tube containing a weighed amount of the substance was broken in 6 *N*-ammonia taken in a stoppered pyrex flask. After the completion of the hydrolysis, the solution was transferred to a platinum basin and evaporated on the water-bath to drive off the excess of ammonia. The residue was then dissolved in water, filtered and the fluorine was then precipitated as calcium fluoride with calcium nitrate. The precipitate was afterwards filtered through a tared glass gooch, washed with water saturated with calcium fluoride, dried at  $120^\circ$  and weighed.

*Ethyl fluocarbonate.*—Ethyl chlorocarbonate (35 g.) was taken in a 100 c.c. flask fitted with a condenser, cooled by iced water. Powdered anhydrous thallous fluoride (74 g.) was introduced into the flask and the mixture well shaken and left for about 12 hours at the

room temperature (27°) with occasional stirring and was then refluxed on a water-bath for 2-3 hours. The product distilled at 57° and was purified by redistillation;  $d_{33}$ , 1.06, yield, 14 g. (47% of the theory). (Found: C, 38.8; H, 5.63; F, 20.81.  $C_3H_5O_2F$  requires C, 39.1; H, 5.43; F, 20.65 per cent).

It is a pungent smelling lachrymatory liquid. It reacts vigorously with ammonia with the formation of ammonium fluoride and urethane. The reaction product is treated with ether from which urethane crystallises out and is identified by its melting point.

*Methyl fluocarbonate.*—Methyl chlorocarbonate (25 g.) was taken in a 100 c.c. flask with a condenser fitted with ice-cold water. Anhydrous thallous fluoride (65 g.) was introduced and the mixture well shaken and kept in an ice-bath for about 6 hours. The flask was then kept at the room temperature for 2-3 hours and finally refluxed at 50°. The product distils at 40°, yield 5 g. (Found: F, 24.53.  $C_2H_3O_2F$  requires F, 24.48 per cent).



# Influence of Temperature and Light Intensity on Photosynthesis and Respiration and an Explanation of "Solarisation" and "Compensation Point"

BY N. R. DHAR.

It is well known that the Arrhenius equation  $\log e K_1/K_2 = A(T_1 - T_2)/T_1 T_2$  is applicable to ordinary chemical reactions taking place in a homogeneous system ( $K_1$  and  $K_2$  are the velocities of the reaction at  $T_1$  and  $T_2$  absolute temperatures and  $A$  is a constant).

In a previous publication (Dhar, *Proc. K. Akad. Wetensch. Amsterdam*, 1920, 23, 44) it was shown that the application of the above Arrhenius relation connecting velocity and temperature of a reaction is certainly more correct than to apply the van't Hoff rule that the temperature coefficient of a chemical reaction for a 10° rise of temperature lies between 2 and 3, because the temperature coefficient does not remain constant at different temperature intervals but falls off with increase of temperature. Moreover, Dhar (*J. Chem. Soc.*, 1917, 111, 707) has shown that for some reactions, the temperature coefficient can have the value 7.2 for a 10° rise.

Many plant physiologists following the lead of Blackman have applied the van't Hoff rule to plant temperature studies. Thus Stiles states, "Many plant and animal processes have been shown to obey the van't Hoff rule, if only approximately and within limits," and "similar curves for the respiration of higher plants have been constructed by Kuijper, who found the van't Hoff rule followed between 0° and 20°" ("Photosynthesis", 1925, p. 100). The application of the Arrhenius relation has been found to be general with ordinary chemical reactions. When the same relation is applied to the results actually obtained regarding the influence of temperature on photosynthesis in plants, it fails, as will be evident from the following table obtained from Warburg's results (*Biochem. Z.*, 1919, 100, 259).

Light intensity.	Observed $\frac{K_1 + 10}{K_2}$	Calc. $\frac{K_1 + 10}{K_2}$
16.	2.0	4.11 between 16° and 25° (taking 4.7 between 5° and 10°)
45	2.1	4.01 between 10° and 20° (taking 4.8 between 5.4 and 10°)
45	1.6	3.66 between 20° and 30° (taking 4.8 between 5.4 and 10°)

The results have been calculated by applying the Arrhenius relation. It appears that the temperature coefficients of photosynthesis do not obey the Arrhenius relation, which has been found to be universally applicable to ordinary chemical reactions investigated so far and no case of failure has been reported. In photosynthesis the observed values are always smaller than the calculated values. The reasons of the non-applicability of this relation to photosynthesis in plants are, (i) the greater influence of temperature on the respiration process than that on photosynthesis, and, (ii) the harmful influence of high temperatures on the chloroplasts.

It has already been stated that when the temperature of a plant system undergoing photosynthesis is increased the velocity of photosynthesis increases but to a smaller extent than that of respiration. Consequently, the temperature coefficient of the observed photosynthesis will appear to be smaller than when the reversible reaction was not present. Moreover, the chloroplast in the protoplasmic cells which is likely to be active in the photosynthetic process starts undergoing deterioration when the temperature is greater than  $20^{\circ}$  and may be partially destroyed when the temperature is still greater. This is evident on comparing the results obtained by Warburg (*loc. cit.*) and those calculated from the Arrhenius relation. The observed temperature coefficients between  $16^{\circ}$  and  $25^{\circ}$  and between  $10^{\circ}$  and  $20^{\circ}$  are nearly half of the calculated values, whilst the observed temperature coefficient between  $20^{\circ}$  and  $30^{\circ}$  is much less than half of the calculated value. The pernicious influence of high temperature on physiological, enzyme, and bacterial processes is well known. In most cases the optimum temperature in these reactions is round about  $20^{\circ}$ . Moreover, in plant photosynthesis, there is an additional factor, namely, the reverse reaction, *e.g.*, respiration, which is also simultaneously going on and is counterbalancing the photosynthetic reaction and hence the influence of temperature on photosynthesis is less pronounced due to these counteracting agencies.

It has already been stated that in the case of some chemical reactions, the temperature coefficient can have the high value 7.2. Hence it is no wonder that the temperature coefficient of photosynthesis at low temperatures (between  $5^{\circ}$  and  $10^{\circ}$ ) has the value 4.3. It seems probable that the photosynthetic reaction is not an adsorption process of which the average temperature coefficient is in the neighbourhood of 1.2 for a  $10^{\circ}$  rise of temperature, but it is controlled by a truly,



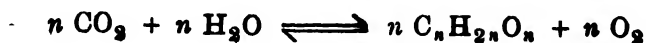
photochemical change having a moderately high temperature coefficient. In several communications from these laboratories it has been shown that photochemical reactions need not have temperature coefficients approaching unity but can have values as high as 4 (cf. Dhar, "Chemical action of light", 1931, pp. 314-318). From the foregoing considerations, it is clear that it is needless to assume that the photosynthetic process involves two reactions. It is believed that in the high light intensity, the chemical reaction ("Blackman reaction" as designated by Warburg) is determining the total velocity of the reaction, because for a rise of temperature between 15° and 25°, the velocity of the photosynthesis is doubled. On the other hand, in low light intensity the temperature coefficient instead of being 2 as with intense light, is 1.06 and hence it has been assumed that the chemical reaction is not the controlling factor as in the previous case; but the photochemical reaction with a low temperature coefficient determines the photosynthetic rate at low intensities of light.

In presence of intense light, the photochemical reaction causing photosynthesis and having a moderately large temperature coefficient, is predominant and the counteracting influence of the respiration process, which is not as much accelerated by light as the photosynthetic reaction, is not prominent. On the other hand, in presence of feeble illumination, the velocity of the photosynthetic reaction is not high, because this reaction takes place only in light and is proportional to the light intensity. In this case, the counteracting influence of respiration, especially at increased temperatures, becomes prominent and hence the influence of temperature on the observed photosynthetic rate is feeble.

Warburg (*loc. cit.*, p. 258) has observed that the temperature coefficient of photosynthesis with the unicellular *alga chorella* is much less when the light intensity is feeble than when it is strong. Thus  $k_t + 10/k_t$  between 16° and 25° with a light intensity 16=2.0, and  $k_t + 10/k_t$  between 15° and 25° with a relative intensity of 1=1.06.

These results which appeared to have been confirmed by other workers can be explained in the following way:

It has already been stated that in a plant, the following opposing reactions are taking place



and the temperature coefficient of photosynthesis is less than that of respiration. Hence, when the light intensity is feeble, the velocity of photosynthesis is small and is slightly greater than that of respiration at the same temperature. Now when the temperature of the system is raised through  $10^{\circ}$  (say), the velocity of the photosynthesis will be increased to a smaller extent than that of respiration. Consequently the temperature coefficient of the observed photosynthesis may be unity or less.

It will be interesting to note in this connection that Harder (*Jahrb. Wiss. Bot.*, 1915, 56, 281) working with low light intensity and sea plants of the polar region obtained the following ratio between photosynthesis and respiration for different temperatures.

20°-22°	0.5382	0.4227	0.4280
2°-8.5°	1.603	0.9207	2.059

Moreover, in nature when the temperature of the air is high, the plants gain no material through photosynthesis because of the high respiration, whilst at lower temperatures with the same light intensity, food materials are formed in the plant.

Willstatter and Stoll ("Kohlensaure Assimilation", 1918) have reported that leaves of low chlorophyll content exhibit a lower acceleration with increasing temperature than the leaves of high chlorophyll content. Thus leaves of *ulmus* with low chlorophyll content showed a temperature coefficient of 1.34 and with a high chlorophyll content of 1.63 between  $15^{\circ}$  and  $25^{\circ}$ . These results of Willstatter and Stoll can be explained from the view point already advanced.

The important researches of Willstatter and Stoll show that although there are minor discrepancies, the rate of photosynthesis is determined by the chlorophyll content of the plant. Hence, in presence of large amounts of chlorophyll in the leaves, the velocity of the photochemical reaction involved in the photosynthetic process will be larger than in the case of leaves containing smaller quantities of chlorophyll. In the case of leaves containing large amounts of chlorophyll, the direct photochemical process being high, the reverse reaction of respiration will appear to be less pronounced and this case is comparable to the case previously discussed with high light intensity, and hence a temperature increase will lead to an increase of photosynthesis. On the other hand, in presence of small amounts of chlorophyll in the leaves, the photosynthetic rate is low and hence the opposing respiration reaction will appear to be prominent and this

case is allied to photosynthesis with low light intensity having small temperature coefficient.

Willstätter and Stoll obtained the following interesting results.

*Photosynthesis of the green and yellow varieties of Elm.*  
5% CO<sub>2</sub> and 24000 Lux.

Variety.	Temp.	Dry wt. of leaves.	Leaf sur- face.	Chlorophyll.	Photosynthesis - CO <sub>2</sub> /hour.	
					8 g. fresh leaves.	1 sq. m. surface
Chlorophyll poor	25°	2.00 g.	321 sq. cm.	0.95mg.	0.075	2.3
„ „	15°	2.00	321	0.95	0.056	1.7
Chlorophyll rich	25°	2.35	421	13.0	0.089	2.1
„ „	15°	2.35	421	13.0	0.058	1.4

The foregoing results show that the temperature coefficient (1.53) of the photosynthesis with chlorophyll-rich leaves is greater than that with chlorophyll-poor leaves (1.34), although the photosynthesis is not at all proportional to the amount of chlorophyll in the leaves. Willstätter and Stoll find that temperature variations do not affect the rate of photosynthesis of the yellow varieties, as much as the normal ones. In the yellow varieties, the amount of photosynthesis being small, the compensating influence of respiration becomes prominent and hence temperature does not appear to influence photosynthesis with these varieties to the same extent as the normal ones with more chlorophyll.

Moreover, differences in light intensity have more profound effect on the yellow varieties than on the normal ones and the time factor appears more slowly than in the normal ones. It is well known that photosynthesis increases with the light intensity and the chlorophyll content of the leaves. Now in the case of leaves containing much chlorophyll, the velocity of photosynthesis will be high and may reach the maximum, even when the light intensity is not high and hence in these cases, the reaction will be less sensitive to the influence of light changes, because the reaction is already fast due to the presence of large amounts of chlorophyll. On the other hand, when the chlorophyll content is small, the reaction velocity is small and light will affect the velocity more markedly than in the previous case. This

explanation is in agreement with the observations of Willstätter and Stoll that in the chlorophyll-rich leaves, an increase of light intensity was without influence on photosynthesis ; in fact the light intensity could be reduced by  $\frac{3}{8}$  without affecting the rate of photosynthesis. Exactly similar exhaustion effect has been observed with several photochemical reactions where the velocity of the reaction may be proportional to  $\frac{1}{2}$  or  $\frac{1}{4}$  in some cases where the reaction is very fast (cf. Bhattacharya and Dhar, *J. Indian Chem. Soc.*, 1929, 6, 197, 523),

*Respiration—the most Fundamental of Plant Processes.*

It seems that in plants, as much as in animals, respiration is the most fundamental process, that is going on in the plant system. Photosynthetic activity is a subsidiary reaction, in comparison with respiration. It appears that the various processes, which are associated with plant life can only take place as long as respiration lasts.

The activity of a plant is measured by its respiration. It appears that the greater the rate of respiration per unit surface, the greater is the activity of the plant. The amount of respiration would depend on (i) the concentration of carbohydrates and other food materials available in the plant, (ii) a minimum oxygen pressure, and, (iii) the activity of the enzymes and inductors. When factors (ii) and (iii) are constant, respiration will depend on the concentration of carbohydrates, proteins and other food materials, which is controlled by the photosynthetic activity of the plant.

The view that respiration is more fundamental in plant life than photosynthesis is supported from the following observations.

Warburg (*Biochem. Z.*, 1919, 100, 264) has reported that, while respiration is not influenced by different partial pressures of oxygen above a certain minimum, photosynthesis is less at higher pressures. A change in the partial pressure of oxygen from  $\frac{1}{50}$  to 1 atmosphere reduces the photosynthetic rate by about  $\frac{1}{3}$ .

Wurmser and Jacquot (*Bull. Soc. Chim. biol.*, 1923, 5, 305; 1924, 6, 169) have observed that when certain marine algae are subjected to temperatures from  $36^{\circ}$  to  $45^{\circ}$  for 1 to 15 minutes, the rate of photosynthesis is always depressed when the plants are returned to the temperature of the environment ( $16^{\circ}$ ). Similar effects are produced with glycerol. Warburg has shown that photosynthetic rate

is reduced by hydrocyanic acid and urethanes in extreme dilutions in which the respiratory activity is not affected and in certain cases, even stimulated. It appears, therefore, that photosynthetic process is more sensitive than that of respiration. As all plant processes depend on respiration, which is the vital reaction in plant life as much as in animal life, photosynthetic activity cannot proceed without respiration taking place in the plant and hence, without the presence of oxygen, which supports respiration in both plant and animal life. Because lack of oxygen is detrimental to respiration, it is also harmful to photosynthesis. Consequently the classical experiments of Boussingoult (*Agronomie chimie agricole et physiologie*, 1868, 4, 329) and Pringsheim (*Sitz. preuss. Akad. Wiss.*, 1887, 763) showing that in an atmosphere of hydrogen, nitrogen, carbon dioxide, or methane, plants lose the power of photosynthesis, are easily explained from the above viewpoint, because in presence of these gases, oxygen respiration stops. It appears, therefore, that besides light, chlorophyll, carbon dioxide and moisture supply, respiration is also necessary for photosynthesis.

Willstätter and Stoll have observed that various plants exhibit a wide variation in their resistance to lack of oxygen. According to Willstätter and Stoll, the partial pressure of oxygen can be reduced to 1/100th of that in air without affecting photosynthesis if the rest of the atmosphere is nitrogen. After complete displacement of oxygen for 2 hours, the leaves on illumination cannot effect photosynthesis, although under these conditions, the leaves show no visible signs of injury. When *cyclamen europaeum*, *polytrichum juniperinum* are exposed to oxygen-free atmosphere for 1 hour, the photosynthetic activity is decreased but not entirely stopped. When the plants are kept in oxygen-free atmosphere for 15 to 24 hours, they show no photosynthesis immediately on illumination, but after  $\frac{1}{2}$  hour or so, photosynthesis begins and continues to a high rate. Long continued exposure to oxygen-free atmosphere produces injurious effects on the photosynthetic mechanism. The longer the time of exposure of a plant to an atmosphere free from oxygen, the lower is the rate of subsequent photosynthesis and more incomplete the recovery. Willstätter and Stoll have concluded from their careful experiments that oxygen is essential for photosynthesis but a small quantity of oxygen is enough. Now, as soon as photosynthesis begins, oxygen is generated and respiration goes on. Lack of oxygen produces a permanent injury

to the plant, because respiration stops in the absence of oxygen.

Moreover, it appears from the foregoing results, that for plants, the oxygen requirements for respiration is less than in animals and they resist lack of oxygen in their living atmosphere much better than animals.

It has already been stated that the activity of a plant is measured by the amount of its respiration per unit surface. Consequently, the greater the respiration, the greater the activity of the plant and greater the photosynthesis, because photosynthesis, like other plant processes, is associated with the activity of the plant. It has already been stated that in plants, Willstätter and Stoll did not find any proportionality between the chlorophyll content and its photosynthetic activity. This is explained from the viewpoint advanced here that the respiratory activity of the plant is the most vital of the plant processes and all other functions of the plant depend on the respiratory activity and consequently, photosynthetic rate is likely to be more directly proportional to the respiratory activity than to any other single factor, e g., chlorophyll content, light intensity or carbon dioxide concentration. Experiments are in agreement with this viewpoint. Plaster (*Beit. Biol. Pflanzen*, 1912, 11, 249) showed that the leaves of the light green or yellow varieties have a lower rate of photosynthesis and respiration than the varieties rich in chlorophyll. Although, there is no parallelism between chlorophyll content and photosynthetic rate, the ratio between respiration and photosynthesis appears to be constant as will be evident from the following results obtained by Plaster with the light green varieties: *ptelea* = 1.77, *catalpa* = 1.72, *mirabilis* = 2.0, *ulmus* = 2, *populus* = 2.1. Similar results correlating respiration and photosynthetic rate have been obtained by Miss Henrici (Inaug. Diss. Basel, 1918, 90, "Chlorophyll Gehalt und Kohlensäure Assimilation bei Alpen-Ebenpflanzen") with alpine and low land plants, Boysen-Jensen (*Bot. tids.*, 1918, 36, 219) and Spoehr and McGee (*Carnegie Inst. of Wash. Pub.* 1923, No. 825, 76).

Willstätter and Stoll have also studied the photosynthetic activity of leaves of different ages. They have compared the activity of a light green leaf from the end of a branch with that of a dark green leaf from the base of the same branch. Their results are given below.

*Photosynthesis of leaves from the same plant but in different stages of development at 25°, 5% CO<sub>2</sub> and 4800 Lux.*

Species.	Date.	Description of leaves.	10 G. fresh leaves.		Photosynthesis g. CO <sub>2</sub> /hour.		Photo-synthetic number
			dry wt.	chlorophyll.	per 1. g. dry wt.	per 1 sq. dm. leaf area.	P <sub>c</sub> .
<i>Acer pseudo-platanus</i>	June 23	4th-6th leaf from end of branch	3.3 g.	8.3mg.	0.030	0.016	11.8°
...	June 24	From base of branch	3.58	40.0	0.058	0.026	5.2
<i>Tilia cordata</i>	June 25	Young light green	2.56	6.5	0.036	0.018	14.2
---	June 26	Lower dark green from same branch	3.19	28.1	0.058	0.028	6.6
<i>Laurus</i>	June 30	Light green leaves	3.10	12.7	0.024	0.019	5.9
<i>Nobilis</i>	July 1	Dark green leaves of previous year	4.15	21.2	0.023	0.023	3.7

The foregoing results of Willstätter and Stoll on the photosynthetic activity of leaves in different stages of development show that although the chlorophyll content of the leaves increases and the photosynthetic activity also increases, the two are not parallel. Consequently, it is clear that with the young leaves, the photosynthetic activity is exceedingly high and is not proportional to their chlorophyll content, because the respiratory activity of the young leaves is also very high. In other words, the greater the respiratory activity (metabolism), the greater is the photosynthetic activity.

The photosynthetic activity of etiolated plants in which the chlorophyll is just developing, shows the disproportionality between photosynthesis and chlorophyll content. Willstätter and Stoll, using cultures of *phaseolus vulgaris* and *zea mays*, found that they are remarkably active, as soon as the first traces of chlorophyll are formed in light. Thus *phaseolus* with a chlorophyll content of 0.7 mg. per 10 grams of fresh leaves, had a photosynthetic number (P<sub>0</sub>) of 138, whilst the control plants grown in light with 18.6 mg. of chlorophyll per 10 g. of leaves showed a photosynthetic number of 9.4. In general, the photosynthetic number of etiolated

leaves is much higher than that of young leaves, which developed in the light. This is certainly due to the fact that the respiratory activity of the etiolated leaves is much greater than that of young leaves which developed in light.

### *Influence of Iron Compounds on Plant Respiration.*

Moreover, the relation of photosynthesis and chlorophyll content of chlorotic plants is of great interest from this point of view. When plants grow in the absence of materials containing iron salts, they become very pale green or colourless with limited development of chloroplasts. This happens even under conditions of high illumination intensity. It has already been emphasised that respiration is the most fundamental and vital of the plant processes and factors, which inhibit respiration, also interfere with normal development and growth of plants. It is well known that iron compounds are of great importance to respiration in the animal kingdom. Dhar and collaborators (*J. Phys. Chem.*, 1925, **29**, 376, 799; 1930, **34**, 711, 737) have shown that food materials are readily oxidised by air or hydrogen peroxide in presence of iron compounds. The iron present in animal blood accelerates the metabolism of food materials in the body. Consequently when the iron content of the blood decreases or the amount of red blood corpuscles becomes less, metabolism of food materials becomes defective; the person suffers from anaemia or chlorosis. Under these circumstances, iron compounds are used as medicine and these help metabolism.

In plant life also, in the absence of iron compounds, respiration becomes defective and hence the vital activities and growth of the plant are hindered and it becomes chlorotic and poor in chlorophyll content. As the respiratory activity is defective in chlorotic plants, it is expected that its photosynthetic power will also be anomalous. This is borne out from the experiments of Willstätter and Stoll, who cultivated plants with nutrient solutions containing no iron. While other types of leaves, also poor in chlorophyll, such as the light green or yellow varieties, autumnal and etiolated leaves, showed high photosynthetic activity in comparison with their chlorophyll content, the chlorotic leaves have a low rate of photosynthesis. Hence photosynthesis goes hand in hand with respiratory activity. It is interesting to note here the



observations of Curtel (*Compt. rend.*, 1900, 130, 1074) who has observed that chlorotic plants have a lower rate of respiration and transpiration than normal plants.

The important fact brought out by the investigation of Willstätter and Stoll is that the leaves of light green or yellow variety, as far as photosynthesis is concerned, are affected more by differences in light intensity, while the leaves rich in chlorophyll are more sensitive to changes of temperature. These results have already been explained in the foregoing pages from our viewpoint of the opposing influence of respiration on photosynthesis.

In explaining these and other results Willstätter and Stoll have been led to the assumption of the existence of an internal factor or protoplasmic factor, which is supposed to be of an enzymatic nature. The author has put forth the view that this internal factor is really the respiratory activity or metabolic activity of the plant, which is also probably of an enzymatic nature and may depend on the presence of inductors.

### *Influence of Age on Plant Processes.*

It is a well established fact that metabolism (carbon dioxide output) per unit area decreases with age in the animal world (cf. Dhar, "New Conceptions in Bio-Chemistry", 1932). In plant kingdom the same relation is observed. From the quantitative work of Willstätter and Stoll on the relations between the rate of photosynthesis, chlorophyll formation and respiration, it is clear that respiratory activity is very high in very young leaves and it decreases with time and development of the leaf. Young leaves have an exceedingly high rate of respiration, which decreases to one-fourth of this rate when the leaf matures. In general, functional activity decreases with age. Under favourable conditions of temperature and light, the development of chlorophyll is rapid. Willstätter and Stoll have observed an increase in photosynthesis with increase in chlorophyll content. There is, however, no direct proportionality between chlorophyll content and photosynthetic rate, as shown in the following table. (Results of Willstätter and Stoll.)

*Rate of photosynthesis, chlorophyll content and photosynthetic number at 25°.*

5 % CO<sub>2</sub>, about 48,000 Lux.

Date.	Species.	From 10 g. leaves.		fresh		Photosynthesis g. CO <sub>2</sub> / hour.		Photosynthetic number P <sub>c</sub> .
		dry wt.	chlorophyll.	dry wt.	chlorophyll.	per g. dry wt.	per 1 sq. dm.	
April 29	<i>Aesculus hippocastanum</i>	2.10 g.	10.1 mg.	0.054	0.043	11.1		
May 7		2.06	15.1	0.088	0.039	12.1		
June 3		2.94	24.7	0.054	0.033	6.4		
Oct 8		3.62	31.2	0.041	0.044	4.8		
May 1	<i>Sambucus nigra</i>	1.85	11.7	0.078	0.046	12.2		
May 8		2.25	23.1	0.101	0.057	9.8		
July 14		2.56	23.5	0.057	0.032	6.2		

With time, the dry weight of the leaves increases and on the basis of the dry weight, there is a decrease in photosynthesis. The leaves also show a consistent increase in chlorophyll content but this does not involve an increase in photosynthesis. Similar results have been obtained with other leaves.

It is well known that the longevity of cold blooded animals is much greater than that of warm blooded ones of the same size. Moreover, amongst warm blooded animals, the longevity of smaller animals is in general less than that of large animals. Also the duration of life varies inversely as the rate of energy expenditure during its continuance. In short, the length of life depends inversely as the rate of living. These results can be explained from the view point that the greater the activity of the cells and the body enzymes, the less is the duration of their active life. It has been frequently noted in catalytic operations that the duration of active catalytic influence of a highly active catalyst is short (*cf.* Dhar, "New Conceptions in Bio-Chemistry", 1932).

These conclusions appear to be applicable to the plant kingdom. In studying the influence of temperature on photosynthesis, it has been observed that the maximum velocity of photosynthesis cannot be maintained for a long time, but that with time, this maximum rate shifts to a lower temperature. This time factor is of great interest in plant physiology. In leaves poor in chlorophyll, i.e., the

light green or yellow varieties, the time factor appears more slowly than in leaves rich in chlorophyll. It has already been stated that chlorophyll-rich leaves are more active towards photosynthesis and respiration than the yellow varieties of leaves. Hence the duration of the activity of the chlorophyll-rich leaves at a definite temperature is expected to be less than that of the comparatively inactive variety of leaves containing smaller amounts of chlorophyll. Consequently, the time factor appears more slowly in the less active yellow leaves than in the active chlorophyll-rich leaves.\* In other words, the activity of the chlorophyll-rich leaf will last for a shorter time than that of the chlorophyll-poor leaf.

### *The Phenomenon of "Solarisation".*

It is well known that not only high temperature but also long exposure to strong light affects photosynthetic activity. Thus Ursprung (*Ber. Bot. Ges.*, 1917, 35, 57) observed that a leaf of *phaseolus* after 5 hours of illumination showed very deep colouration of the starch iodine, while after 8½ hours illumination, the reaction was faint. This phenomenon can be observed with almost any source of light of sufficient intensity and the time required is proportional to the light intensity. The effect is first brought about in the red orange portion, the region showing the best photosynthetic activity. With higher intensity, the shorter wave-lengths bring about in shorter time and it is apparently proportional to the photosynthetic activity of light. Ursprung (*loc. cit.*) has called this phenomenon "solarisation," as it is analogous to the phenomenon of polarisation observed in photographic plates under similar circumstances.

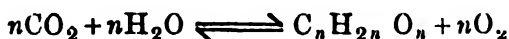
It is expected that not only with starch but with other carbohydrates, similar effect will be observed. This behaviour has been ascribed to the inactivation of chloroplasts. After long exposure to intense light, the plant organs are assumed not to function, although they are not killed and on keeping in the dark for a period, again produce starch normally.

The inhibiting effect of long exposure to light of high intensity on photosynthesis has also been studied by Ewart (*Ann. Bot.*, 1897, 11, 499; 1898, 12, 379) and the inhibiting effect has been ascribed to the destruction of chlorophyll. Pantanelli (*Jahrb. Wiss. Bot.*, 1903, 29, 167) explains the fatigue effects observed by him in bright

light from the view points of chlorophyll destruction and injury to the chloroplast plasma. The observations of Ewart on *allium cepa*, which does not form starch, indicate that when leaves of this plant are exposed to bright light for 14 days or for a shorter period while being fed with sugar, the evolution of oxygen finally ceases. This inactivation apparently does not injure the cells or chloroplasts. After a few days in darkness, the capacity for photosynthesis is regained.

The foregoing facts are explained from the following considerations.

In plants the following equilibrium exists :



The direct action (photosynthesis) is being opposed by the reverse reaction (respiration), which will increase, according to the law of mass action, with increase in the concentration of the carbohydrate, which is a product of photosynthesis. Consequently with accumulation of carbohydrates or when the plants are fed with sugar, as was done by Ewart, photosynthesis is retarded and may stop altogether when the carbohydrate content becomes very high. When the illumination is high and it lasts for a long time, the carbohydrate content increases and along with it the respiration also increases, and thus the photosynthetic velocity falls off with time even when the illumination is continued. After a time, the respiration will more than counterbalance photosynthesis and the carbohydrates formed by the photosynthesis will be oxidised to carbon dioxide and water and will disappear on prolonged exposure. When the carbohydrates disappear, the photosynthesis will again begin. It has been known for a long time that the photosynthetic rate decreases with accumulation of the products of photosynthesis. Moreover, Saposchnikoff (*Ber. Bot. Ges.*, 1893, 11, 391) has demonstrated the inhibitory power of an accumulation of carbohydrates and that these cannot increase beyond a certain point. When the leaves of *vitis vinifera* contain 23 to 29% carbohydrates of the dry weight, photosynthesis ceases and respiration predominates. Saposchnikoff has shown that as carbohydrates accumulate, decrease of photosynthetic rate takes place, whilst a decrease in the carbohydrate content results in an increased photosynthesis. These results are evident from the view point of the reversible reactions already put forward.

Moreover, there are two other factors, which increase respiration, should be considered *viz.*, (i) influence of light intensity on the respiratory process, and (ii) influence of increased temperature caused by prolonged light absorption. In several publications, Dhar and collaborators (*J. Phys. Chem.*, 1925, 29, 926; 1928, 32, 1263; 1930, 34, 993) have shown that food materials like starch, sugars, proteins, fats, etc., in aqueous solutions or suspensions are oxidised to carbon dioxide and water by simply passing air at the ordinary temperature in presence of sunlight. In absence of light, there is no oxidation. In presence of inductors like ferrous hydroxide cerous hydroxide, etc., the food materials are oxidised to carbon dioxide and water by air even in absence of light. In presence of sunlight, these oxidations are greatly increased. Hence, Dhar and collaborators have suggested that on light exposure the metabolism in the animal body is increased, because the food materials are oxidised to a great extent by air due to the absorption of light. It seems pretty certain that in plants also the respiration or the oxidation of carbohydrates and other food materials, which slowly proceeds in the dark due to the presence of enzymes and inductors, is accelerated on exposure to light. It is well known that several plants and flowers run a temperature higher than that of the surrounding air in the dark due to respiration (*cf.* Kostycher, 'Plant Respiration', 1927, p. 12) and these may be roughly compared to warm blooded animals. In the dark, most plants resemble cold blooded animals and they undergo oxidation and the carbohydrates and other food materials are burnt away. In presence of strong light, the respiration velocity seems to be increased. Moreover, when the plant is exposed to strong light for a long time, the temperature of the plant is likely to increase and with increased temperature, the respiration velocity is markedly increased, because the influence of temperature seems to be more pronounced on respiration than on photosynthesis. Consequently, when a plant is exposed to bright light for a long time, respiration more than counterbalances photosynthesis due to the increased concentration of carbohydrates, increased velocity of respiration by the absorption of radiant energy in the form of light and increase in the temperature of the plant by the absorption of light and the conversion of the light rays to heat. Under these circumstances, plants may behave as animals, as far as metabolism is concerned.

*Compensation Point.*

The compensation point, *i.e.*, the light intensity at which the photosynthetic and respiratory activities of the plant compensate each other decreases with decrease of temperature as will be evident from the following table.

Name.	Intensity at 20°.	Intensity at 5°.
<i>Spirogyra</i>	174	26.7
<i>Fontinalis</i>	150	40
<i>Cladophora</i>	253.3	62.9
<i>Cinclidotus</i>	400	75

The foregoing results show that the light intensity which at 20° represented the compensation point produced an evolution of oxygen due to photosynthesis at 5°

With *Cladophora*, with increasing temperature, the compensation point rises more rapidly than the rate of respiration determined in the dark; an increase of temperature from 5° to 25° causes the respiration to become 4.8 times greater in the dark, whilst the light intensity increases to 6.69 times.

The foregoing results as well as other facts on the compensation point can be explained from the following considerations: (a) Photosynthesis is proportional to the light intensity, there being no photosynthesis in the dark. (b) Respiration takes place in the dark but is appreciably accelerated by light. (c) An increase of temperature affects respiration more markedly than photosynthesis.

The fact that the compensation point rises with increase of temperature is due to the greater increase of respiratory activity than photosynthetic activity with increased temperature. The respiratory activity of the plant, which counterbalances the photosynthetic process, increases much more than photosynthesis at higher temperatures and consequently the light intensity must be increased to cause more photosynthesis to counteract the increased respiratory activity. There is another reason for further increase in the respiratory activity of the plant. Hitherto, it has been assumed by most of the plant physiologists that the process of respiration is not accelerated by light. But it is evident from the researches of Dhar and collaborators that animal metabolism is markedly accelerated by light absorption. Hence, it seems pretty certain that the res-

piratory process taking place in plants is also accelerated by light. Consequently, the respiratory activity of the plant is accelerated by two agencies, *e g.*, temperature and light intensity and thus the light intensity required for increased photosynthesis in order to counteract this high respiratory activity should be very high. Thus with increasing temperature, the compensation point should rise more rapidly than the rate of respiration because of its additional enhancement by light absorption and this is clearly borne out from the experiments on *cladophora* in which an increase of temperature from 5° to 25° causes the respiration to become 4·8 times greater when determined in the dark, whilst the light intensity increases 6·69 times for the compensation point.

It is evident that under certain circumstances, when the temperature is high and the light is intense, the compensation point may not be attained even with intense light and the plant will evolve carbon dioxide like an animal even in presence of light. This is likely to happen frequently in tropical countries where at the sea level, the heat rays of the sun become very prominent and the temperature of the plant will be high and photosynthesis cannot counterbalance respiration under these circumstances. At higher altitudes, the light rays are more active than at the sea level and it is expected that at these altitudes, very seldom, respiration will exceed photosynthesis in sunlight. These conclusions are corroborated from the experimental results of Harder (*Jahrb. Wiss. Bot.*, 1921, 60, 531) with sea plants in the polar zones where the light intensity is not very high (*vide* Harder's data recorded in p. 544). The position of the compensation point of a plant with reference to temperature is naturally of great importance to the life of the plants and its relation to the environment.

Harder has reported that conditions may exist in nature where at higher temperatures, the plant stores no material through photosynthesis on account of the high respiratory activity. While at lower temperatures with the same light intensity, food materials are formed in the plant by photosynthesis.

The experimental observation that compensation point varies with different plants is explained on the basis that the respiratory activity of the plant and its increment by temperature and light vary with different plants.

Starting with the same culture of *cladophora*, and keeping one portion in diffused light and another in direct sunlight, great differ-

ences in the compensation point are observed in a week. With *sinapis alba*, a plant growing in light, the compensation point is at 1.0 (Bunsen units  $\times 100$ ) but a compensation point lying at only 0.2 is observed with *oxalis acetosella*, a shade plant. Previous illumination of the plant must be considered before any conclusion is drawn from determination of the compensation point, which varies considerably with previous illumination of the plant. It has been observed that under certain circumstances in *fontinalis*, photosynthesis more than counterbalances respiration when the illumination is only 10 Lux, whilst under other conditions, 150 Lux is insufficient to achieve this.

Under constant and high illumination, leaves of beach trees emit carbon dioxide at 6250 Lux; the sun trees, *robina*, requires 25 times more intense light for photosynthesis to exceed respiration than the shade tree *fagus*.

These experimental observations are explicable by considering the temperature of the trees growing in light is higher than that of trees growing in the shade. Hence, the respiratory activity of plants growing in shade is much less than that growing in light. Moreover, the respiration of plants growing in light is also accelerated by the light absorption. Consequently the light intensity required to cause the increased photosynthesis in order to counteract the enhanced respiration due to an increase of temperature and light absorption must be very high.

Moreover, there is another important consideration in the explanation of the higher compensation point of trees grown in light than in the shade. From our experience on the velocity of photochemical reactions taking place in strong light, it is generally observed that the velocity of the photochemical reaction is not directly proportional to the light intensity or the absorbed light but the velocity varies as  $I^n$  where  $n$  is less than unity. On the other hand, in presence of feeble light, the velocity varies as  $I^n$ , where  $n$  is unity or more. Consequently, from the quantitative experiments with ordinary photochemical reactions, it is clear that in presence of intense light, photochemical reactions utilise less amount of absorbed radiation than when the same reactions take place in less intense light. This is usually known as "exhaustion effect." It is clear, therefore, that in photosynthesis, the same relation is to be expected. This behaviour has been observed by Warburg (*Z. physikal. Chem.*, 1922, 102, 246) in his experiments



on the efficiency of the photosynthetic process. It has been reported by Warburg that when plants are cultivated under conditions of high light intensity, they utilise only a small amount of the absorbed energy. Plants grown under conditions of low light intensity can utilise a relatively large proportion of the absorbed energy. Hence, the light intensity necessary to obtain the requisite velocity of photosynthesis required to counteract respiration in the case of plants growing in light will be greater than that required for plants cultivated in the shade. Hence by growing the same type of plant under conditions of high and low light intensity, one type apparently passes into the other within a short time and its photosynthetic efficiency and possibly respiratory activity are altered.

From the foregoing pages, it is clear that the contention of Plaetzer (*Verhandlungen Physik-Med Ges.*, Würzburg N. F., 1917, 45, 31), that the value of the light intensity at the compensation point is not a function of the respiratory activity is not correct. Plaetzer in his consideration of the compensation point missed the important point that the respiratory activity is also accentuated by light and that it is more influenced by temperature than photosynthesis.

From these considerations one thing comes out very prominently that respiration is of vital importance to plants and is more fundamental and important to plant life than photosynthesis, which predominates in the plant only under highly restricted conditions of temperature and light intensity. In other conditions beyond this limit, in light as well as in the dark, plant life enjoys respiratory activity as much as animal life. Hence it appears that respiratory activity controls plant life as animal life.

#### SUMMARY.

1. The Arrhenius relation connecting velocity and temperature of a reaction which is applicable to ordinary chemical reactions, is not valid in the case of the influence of temperature on photosynthesis in plants. The non-applicability of the Arrhenius relation to photosynthesis and many other phenomena in plant life can be explained from the following considerations:

(a) It appears that in plant life, the following opposing reactions are taking place,



The direct action (photosynthesis) is being opposed by the reverse reaction (respiration) which increases according to the law of mass action with increase in the concentration of carbohydrates formed from photosynthesis.

(b) There is reason to believe that the velocity of respiration in plants is appreciably accelerated by light.

(c) The influence of temperature on respiration appears to be greater than that on photosynthesis.

2. The greater influence of temperature on photosynthesis in presence of strong light than that in weak light can be explained from the foregoing considerations. Hence, it is needless to assume that there are two reactions involved in photosynthesis.

3. The observations of Willstatter and Stoll that *leaves of low chlorophyll content* show a lower acceleration of photosynthesis with increase in temperature than the leaves of high chlorophyll content, have also been explained from the same point of view

4. The experiments of Willstatter and Stoll showing that in chlorophyll-rich leaves an increase of light intensity does not affect photosynthesis have been explained from the view point of "exhaustion effect" as observed in ordinary photochemical reactions.

5. That oxygen is essential for photosynthesis appears to be due to the fact that plant life depends on oxygen respiration and the activity of the plant and along with it its photosynthetic power depend on its respiratory activity.

6. The photosynthetic activity is exceedingly high in young leaves and is not proportional to the chlorophyll content. This is because that the respiratory activity of young leaves is very high. In plant life, as well as in animal life, metabolism decreases with age.

7. In plant life in the absence of iron compounds, respiration and photosynthesis become defective as in chlorotic plants, because iron compounds accelerate respiration.

8. It appears that the factor which really controls plant life is its respiratory or metabolic activity.

9. In the animal world, the length of life depends inversely as the rate of living. The duration of the catalytic activity of an active catalyst appears to be short. These considerations are applicable to plant life as well. In leaves poor in chlorophyll, the time factor appears more slowly than in chlorophyll-rich leaves. In other words, the activity of chlorophyll-rich leaves would last for a shorter period than that of chlorophyll-poor leaves.

10. The phenomenon of "solarisation", that is, the disappearance of carbohydrates formed from photosynthesis, after prolonged illumination appears to be due to respiration, that is, their oxidation by oxygen in presence of light. The respiration, that is, the oxidation of carbohydrates is also increased by increase of temperature caused by light absorption.

11. The compensation point, that is, the light intensity at which the photosynthetic and respiratory activity of plants compensate each other, decreases with decrease of temperature. A certain light intensity which at 20° represents the compensation point, causes an evolution of oxygen due to photosynthesis at 5°. In nature, under certain conditions and at high temperatures, the plant cannot store any material due to photosynthesis on account of high respiratory activity, whilst at low temperatures, the same light intensity, food materials are formed by photosynthesis. The above results have been explained from the following considerations. (i) Photosynthesis is proportional to the light intensity, there being no photosynthesis in dark. (ii) Respiration takes place in the dark but is appreciably accelerated by light. (iii) An increase in temperature affects respiration more markedly than photosynthesis.

12. Respiration appears to be the more fundamental reaction in plant and is more important to plant life than photosynthesis, which predominates in plants only under restricted conditions of temperature and light intensity.

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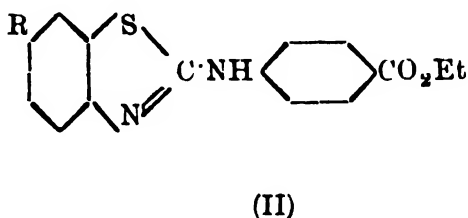
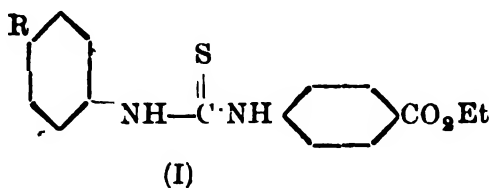
**The Directive Effect of Substituents on the Cyclisation  
of Substituted *s*-Diarylthiocarbamides. . Part III.  
The Effect of the Carbethoxy Group on the  
Formation of Anilinobenzthiazoles,  
from *p*-Carbethoxy-*s*-Diphenyl-  
thiocarbamides and Bromine.**

BY MOHAMMAD OMAR FAROOQ AND ROBERT FERGUS HUNTER.

It has been shown in the course of earlier investigations that the nitro and cyano groups in *p*-substituted-*s*-diphenylthiocarbamides do not direct thiazole cyclisation by bromine in the sense opposite to that of *o*:*p*-directive substituents, but give rise to anilinobenzthiazole derivatives in which the *meta*-directive substituent appears in the 1-arylamino grouping (Hunter and Jones, *J. Chem. Soc.*, 1930, 2190; Hunter, *J. Indian Chem Soc.*, 1932, 9, 436). The *meta*-directive properties of these two groups have been attributed to the presence of the semipolar double bond in the former, the positive end of which tends to attract electrons from all parts of the molecule, and to the tendency of the system of the six electrons which are mutually shared between two atomic nuclei in the latter to attract additional electrons in order to obtain a more stable association of eight or ten electrons (Baker, Cooper and Ingold, *J. Chem. Soc.*, 1928, 426). It, therefore, appeared of interest to examine the effect of the carbethoxy group whose *meta*-directive tendencies are ascribed to the "electron sink" properties of the carbonyl group (Allan, Oxford, Robinson and Smith, *J. Chem. Soc.*, 1926, 401) on the thiazole cyclisation of *p*-substituted-*s*-diphenylthiocarbamides.

As might be anticipated, *p*-carbethoxy-*s*-diphenylthiocarbamide (I, R=H) gave rise on treatment with bromine under moderately vigorous conditions to ethyl 1-anilinobenzthiazole-4'-carboxylate (II, R=H), whose constitution was established by synthesis from 1-chlorobenzthiazole and ethyl *p*-aminobenzoate. On prolonged bromination in the presence of excess of the halogen, however, nuclear substitution occurred with the production of ethyl 5-bromo-1-anilinobenzthiazole-4'-carboxylate (II, R=Br), whose orientation

follows from its synthesis from 1-chloro-5-bromobenzthiazole and ethyl *p*-aminobenzoate. Curiously enough, although we were able to show the formation of ethyl 5-bromo-1-anilinobenzthiazole-4'-carboxylate in the reaction between *s*-*p*-carbethoxyphenyl-*p*-bromophenylthiocarbamide (I, R=Br) and bromine, it was not found possible to isolate the base in a condition of purity in this reaction.



*s*-*p*-Carbethoxyphenyl-*p*-tolylthiocarbamide (I, R=Me) behaved similarly and yielded ethyl 1-anilino-5-methylbenzthiazole-4'-carboxylate (II, R=Me), identical with that obtained from 1-chloro-5-methylbenzthiazole and ethyl *p*-aminobenzoate.

Difficulties similar to those encountered in the synthesis of ethyl 5-bromo-1-anilinobenzthiazole-4'-carboxylate from *s*-*p*-carbethoxyphenyl-*p*-bromophenylthiocarbamide were also experienced in connexion with the bromination of *s*-*p*-carbethoxyphenyl-*p*-chlorophenylthiocarbamide, which gave rise to specimens of ethyl 5-chloro-1-anilinobenzthiazole-4'-carboxylate (II, R=Cl) which could not be completely purified by recrystallisation. The 5-chloro-1-anilinobenzthiazole was, however, obtained in a satisfactory condition of purity from the condensation of ethyl *p*-aminobenzoate with 1:5-dichlorobenzthiazole (III), which was synthesised from 5-chloro-1-aminobenzthiazole by means of the Sandmeyer reaction (*cf.* Hunter and Jones, *loc. cit.*).

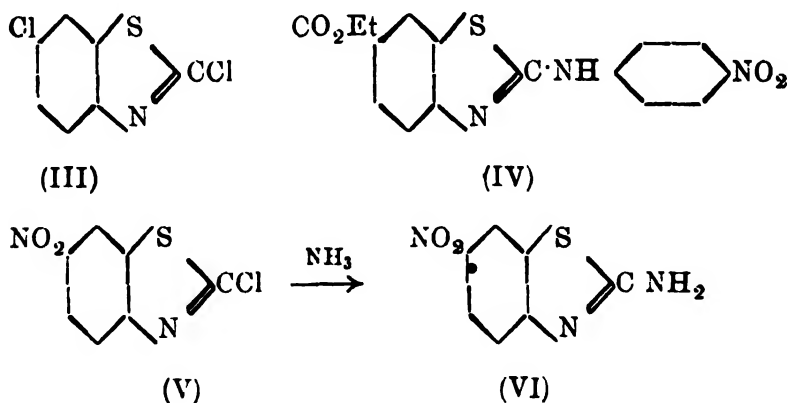
It is, therefore, evident that the effect of the carbethoxy group falls well into line with that of the other *meta*-directive substituents previously examined, and particular interest therefore attaches itself to the bromination of *s*-*p*-carbethoxyphenyl-*p*-nitrophenylthiocarbamide, in which the inhibitory effects of the two *meta*-directing groups

are in opposition:  $\text{EtO} \cdot \text{CO} \text{---} \text{C}_6\text{H}_4 \text{---} \text{NH} \cdot \text{CS} \cdot \text{NH} \text{---} \text{C}_6\text{H}_4 \text{---} \text{NO}_2^+$ .

This thiocarbanilide might clearly give rise either to ethyl 5-nitro-1-anilinobenzthiazole 4'-carboxylate (II,  $\text{R}=\text{NO}_2$ ), or to ethyl 4'-nitro-1-anilinobenzthiazole-5-carboxylate (IV), according to the thiazole cyclisation by bromine. The former base was readily synthesised from ethyl *p*-aminobenzoate and 5-nitro-1-chlorobenzthiazole (V), obtained by direct nitration of 1-chlorobenzthiazole (Hofmann, *Ber.*, 1880, **13**, 11), which was orientated by its conversion by ammonia into 5-nitro-1-aminobenzthiazole (VI), whose formula has been established by rational synthesis from *p* nitrophenylthiocarbamide and bromine (Hunter and Jones, *loc. cit.*).

An attempt to synthesise 5-nitro-1-chlorobenzthiazole from *p*-nitrophenylthiocarbimide and phosphorus pentachloride (*cf.* Hofmann, *loc. cit.*) proved unsuccessful, the reaction being accompanied by considerable decomposition and charring.

Bromination of *s-p*-carbethoxyphenyl-*p*-nitrophenylthiocarbamide gave rise to a base isomeric with ethyl 5-nitro-1-anilinobenzthiazole-4'-carboxylate, which is evidently the 4'-nitro derivative (IV).



The effect of the positive pole in the nitro group, therefore, outweighs the "electron sink" capacity of the carbonyl group in *s-p*-carbethoxyphenyl-*p*-nitrophenylthiocarbamide, thiazole cyclisation taking place in this case on the nucleus which carries the *meta*-directive carbethoxyl group.

#### EXPERIMENTAL.

*p*-Carbethoxyphenylthiocarbimide (Hunter and Parken, *J. Indian Chem. Soc.*, 1932, **9**, 859) is best purified by recrystallisation from

petroleum-benzene in which the di-*p*-carbethoxyphenylthiocarbamide, formed as a by-product, is nearly insoluble.

*p*-Carbethoxy-*s*-diphenylthiocarbamide (I, R=H), prepared by the condensation of the carbethoxyphenylthiocarbimide (2.1 g.) and aniline (1 c.c.) in alcohol or in benzene, crystallised in soft silky flakes, m.p. 129-80°. (Found: S, 11.0.  $C_{16}H_{16}O_2N_2S$  requires S, 10.7 per cent).

*Ethyl 1-anilinobenzthiazole-4'-carboxylate* (II, R=H). (i) *Synthesis from 1-chlorobenzthiazole and ethyl p-aminobenzoate*.—A mixture of 1-chlorobenzthiazole (1 g.) and ethyl *p*-aminobenzoate (1 g.) was gently heated in an open Pyrex boiling tube over a small luminous flame until a violent reaction occurred and the product was basified with ammonia. On crystallisation from alcohol-ethyl acetate, ethyl 1-anilinobenzthiazole-4'-carboxylate was obtained in small crystals, m.p. 182-83°. (Found: S, 10.9.  $C_{16}H_{14}O_2N_2S$  requires S, 10.7 per cent).

(ii) *The action of bromine on p-carbethoxy-s-diphenylthiocarbamide*.—The thiocarbamide (0.7 g.) in chloroform (10 c.c.) was treated with bromine (0.8 c.c. in 1 c.c. of chloroform) and the mixture was heated on a steam-bath under reflux for 20 to 25 minutes. The evolution of hydrogen bromide commenced after the first two minutes, heating continued vigorously for a further five minutes, and then gradually abated. On cooling, a red *hydroperbromide* crystallised, which was collected on porous earthenware, dried in a vacuum and added to saturated sulphurous acid (100 c.c.) The suspension was treated with sulphur dioxide and the mixture was kept overnight to ensure complete reduction. On basification with ammonia and recrystallisation from alcohol ethyl 1-anilinobenzthiazole-4'-carboxylate was obtained, m.p. 175-76° alone and m.p. 180-83° when mixed with the specimen obtained from 1-chlorobenzthiazole and ethyl *p*-aminobenzoate.

*Ethyl 5-bromo-1-anilinobenzthiazole-4'-carboxylate* (II, R=Br). (i) *Synthesis from 1-chloro-5-bromobenzthiazole and ethyl p-aminobenzoate*.—1-Chloro-5-bromobenzthiazole which was originally prepared by Dyson, Hunter and Soyka (*J. Chem. Soc.*, 1929, 458) in 2% yield from *p*-bromophenylthiocarbimide and phosphorus pentachloride is much more conveniently prepared in quantity from phenylthiocarbamide by means of the following steps: 1-Aminobenzthiazole  $\rightarrow$  5-bromo-1-aminobenzthiazole  $\rightarrow$  1-chloro-5-bromobenzthiazole. The aminobenzthiazole (20 g.) was dissolved in warm chloroform



(180 c. c.) and the solution was cooled in ice and stirred during the addition of bromine (9 c.c. in 10 c. c. of chloroform). The precipitate was collected, dried on porous earthenware in a vacuum, added to saturated sulphurous acid, and sulphur dioxide was passed through the mixture until decolorisation was complete. On basification and recrystallisation from alcohol, 5-bromo-1-aminobenzthiazole was obtained, m. p. 208-10° which is quite pure enough for the next stage, yield 80-90%. 5-Bromo-1-aminobenzthiazole (25 g.) was treated with 110 c.c. of hydrochloric acid (5-6 %), and the mixture was cooled to 0° and diazotised with sodium nitrite (12.5 g in 30 c. c. of water). Concentrated hydrochloric acid (200 c.c.) was then added, and the mixture was boiled for 5 minutes and the 1-chloro-5-bromobenzthiazole isolated by distillation in steam. After recrystallisation from alcohol, the chlorothiazole had m. p. 101-102°, yield 7-8 g. Dyson, Hunter, and Soyka recorded the m. p. of 1-chloro-5-bromobenzthiazole, prepared from *p*-bromophenylthiocarbimide and phosphorus pentachloride as 89°. An intimate mixture of 1-chloro-5-bromobenzthiazole (0.56 g) and ethyl *p*-aminobenzoate (0.5 g.) was heated until condensation took place and the product was basified with ammonia and kept overnight. On recrystallisation from alcohol-ethyl acetate, ethyl 5-bromo-1-anilinobenzthiazole-4'-carboxylate was obtained in small crystals, m. p. 227-28°. (Found: Br, 21.1 C<sub>16</sub>H<sub>13</sub>O<sub>2</sub>N<sub>2</sub>BrS requires Br, 21.2 per cent).

(ii) *Prolonged bromination of p-carbethoxy-s-diphenylthiocarbamide.*—Bromine (1 c.c. in 1 c.c. of chloroform) was added to the carbethoxydiphenylthiocarbamide (0.5 g. in 10 c.c. of the same solvent) and the mixture was heated under reflux on a steam-bath for an hour. The bromo-addition compound was reduced in the usual way and the product recrystallised from methyl alcohol, when ethyl 5-bromo-1-anilinobenzthiazole-4'-carboxylate was obtained which had m.p. 226°, and m.p. 226-28° when mixed with the specimen obtained from 1-chloro-5-bromobenzthiazole and ethyl *p*-aminobenzoate.

(iii) *The action of bromine on s-p-carbethoxyphenyl-p-bromophenylthiocarbamide.* — *s-p*-Carbethoxyphenyl-*p*-bromophenylthiocarbamide was prepared by mixing solutions of *p*-bromoaniline in benzene (1.7 g. in 8 c.c.) and *p*-carbethoxyphenylthiocarbimide in benzene (2.1 g. in 10 c.c.), and concentrating the resulting solution on a steam-bath. The thiocarbamide was washed with petroleum-benzene

and thereafter recrystallised from benzene, from which it separated in glistening plates, m.p. 158-59°, yield 1.8 g. (Found: S, 8.7.  $C_{16}H_{15}O_2N_2$  BrS requires S, 8.4 per cent). A solution of the carbethoxyphenylbromophenylthiocarbamide (0.5 g.) in chloroform (10 c. c.) was treated with bromine (1 c. c. in 1 c. c. of chloroform) and the mixture was heated under reflux for  $\frac{1}{2}$  hour, cooled, and the bromo-addition compound was dried in a vacuum and reduced with sulphurous acid in the usual way. On recrystallisation from alcohol, ethyl 5-bromo-1-anilinobenzthiazole-4'-carboxylate, was obtained, m.p. 188-90° mixed m.p. with an authentic specimen being 190-92°. Several experiments were carried out in which both the quantity of chloroform used as solvent for bromination, and the time of heating was varied, but in no case was a product of melting point higher than 192-93° isolated. Attempts to raise the melting points of such products by varying the solvents used for recrystallisation proved equally fruitless.

*Ethyl 1-anilino-5-methylbenzthiazole-4'-carboxylate* (II, R=Me).

(i) 1-Chloro-5-methylbenzthiazole was conveniently prepared from 1-amino-5-methylbenzthiazole by means of the Sandmeyer reaction (. unter and Jones, *loc. cit.*), and crystallised from alcohol in glistening needles, m. p. 49-50°. Ethyl-1-anilino-5-methylbenzthiazole-4'-carboxylate, prepared by condensing equimolecular proportions of 1-chloro-5-methylbenzthiazole and ethyl *p*-aminobenzoate under the usual conditions, separated from alcohol—ethyl acetate in small crystals, m. p. 206-207°. (Found: S, 10.6.  $C_{17}H_{16}O_2N_2S$  requires S, 10.8 per cent).

(ii) *The action of bromine on p-carbethoxyphenyl-p-tolylthiocarbamide.*—*p*-Carbethoxyphenyl-*p*-tolylthiocarbamide was prepared by the condensation of equimolecular proportions of *p*-carbethoxyphenylthiocarbamide and *p*-toluidine in benzene solution, washed with petroleum-benzene and recrystallised from boiling benzene. It formed glistening plates, m. p. 160-61°. (Found: S, 10.2.  $C_{17}H_{16}O_2N_2S$  requires S, 10.2 per cent). The carbethoxyphenyltolylthiocarbamide (0.5 g.) in chloroform (10 c. c.) was treated with bromine (0.6 c. c. in 1 c. c. of chloroform) and the mixture was heated under reflux for 15 minutes. The evolution of hydrogen bromide which was copious after the first two minutes' heating abated after 10 minutes. The solution was cooled in ice and the red crystalline hydroperebromide was dried in a vacuum and reduced in the usual way by sulphurous acid and sulphur dioxide. On basification and recrystallisation from

alcohol-ethyl acetate, ethyl 1-anilino-5-methylbenzthiazole-4'-carboxylate was obtained which had m.p. 206°, and m.p. 206-207° when mixed with the specimen prepared from 1-chloro-5-methylbenzthiazole and ethyl *p*-aminobenzoate.

*Ethyl 5-chloro-1-anilinobenzthiazole-4'-carboxylate* (II, R=Cl).

(i) *Synthesis from 1:5 dichlorobenzthiazole and ethyl *p*-aminobenzoate.* 1:5—*Dichlorobenzthiazole*.—6.2 G. of 5-chloro-1-aminobenzthiazole (Dyson, Hunter and Morris, *J. Chem. Soc.*, 1927, 1186) were treated with hydrochloric acid as in the case of the 5-bromo derivative, and diazotised with sodium nitrite (8.1 g.) at 0° and the diazonium salt was treated with concentrated hydrochloric acid and the mixture was boiled. The *dichlorobenzthiazole*, isolated by steam distillation, crystallised from alcohol in needles, m.p. 101°, yield 2.8 g. (Found: Cl, 35.1.  $C_7H_3NCl_2S$  requires Cl, 34.8 per cent). *Ethyl 5-chloro-1-anilinobenzthiazole-4'-carboxylate*, prepared from the condensation of an equimolecular mixture of 1:5-dichlorobenzthiazole and ethyl *p*-aminobenzoate had m.p. 226°. (Found: Cl, 10.5.  $C_{16}H_{13}O_2N_2ClS$  requires Cl, 10.7 per cent).

(ii) *The action of bromine on s-p-carbethoxyphenyl-p-chlorophenylthiocarbamide.* *s-p-Carbethoxyphenyl-p-chlorophenylthiocarbamide*, prepared by condensation of *p*-carbethoxyphenylthiocarbimide (2.1 g.) and *p*-chloroaniline (1.2 g) in benzene, separated from a comparatively large volume of benzene in plates, m.p. 159-60°, yield 1.8 g. (Found: S, 9.7.  $C_{16}H_{15}O_2N_2ClS$  requires S, 9.6 per cent). The carbethoxyphenylchlorophenylthiocarbamide (0.5 g.) in chloroform (10 c.c.) was treated with bromine (1 c.c. in 1 c.c. of chloroform) and the mixture was heated under reflux for  $\frac{1}{4}$  hour. The hydroperbromide was dried in a vacuum and reduced with sulphurous acid and sulphur dioxide in the usual way. On basification and recrystallisation from alcohol, ethyl 5-chloro-1-anilinobenzthiazole-4'-carboxylate was obtained which had m.p. 178° and m.p. 179-201° when mixed with the specimen prepared from the dichlorobenzthiazole and ethyl *p*-aminobenzoate. In a similar experiment in which the carbethoxyphenylchlorophenylthiocarbamide (0.45 g) in chloroform (10 c.c.) was treated with bromine (0.9 c.c. in 1 c.c. of chloroform), and heating under reflux was continued for 43 to 45 minutes, a bromo-addition compound was obtained which on reduction and recrystallisation of the resulting anilinobenzthiazole gave a crop of crystals which had m.p. 188° and m.p. 190-201° when mixed with a genuine specimen. All attempts to purify this product by further fractional crystallisation, however, proved unsuccessful.

*Synthesis of ethyl 5-nitro-1-anilinobensthiazole-4'-carboxylate* (II,  $R=NO_2$ ). (i) *Nitration of 1-chlorobensthiazole and the orientation of 5-nitro-1-chlorobensthiazole by its conversion into 5-nitro-1-aminobensthiazole*.—Chlorobensthiazole (prepared by the Sandmeyer method from 1-aminobensthiazole) was gradually added drop by drop with stirring to fuming nitric acid ( $d\ 1.5$ , 10 vols.) cooled in a freezing mixture. The solution was kept for a short time and then poured into a large volume of water and the precipitated nitrochlorobensthiazole was collected and recrystallised from ethyl acetate, from which it separated in yellow needles, m.p.  $190^\circ$  (*cf.* Hofmann, *loc. cit.*). The nitrochlorobensthiazole (0.2 g.) was heated with ammonia ( $d\ 0.880$ , 2.5 c.c.) in a sealed tube at  $150$ – $160^\circ$  for 6 to 7 hours and the product was collected and recrystallised from alcohol, when 5-nitro-1-aminobensthiazole was obtained which had m.p.  $242$ – $43^\circ$  alone and when mixed with an authentic specimen prepared in an earlier investigation (Hunter and Jones, *loc. cit.*). The identity was further confirmed by conversion of the 5-nitro-1-aminobensthiazole into its pale yellow acetyl derivative by means of acetic anhydride, which had m.p.  $292^\circ$  alone and when mixed with an authentic specimen. (ii) *Synthesis of ethyl 5-nitro-1-anilinobensthiazole-4'-carboxylate from 5-nitro-1-chlorobensthiazole and ethyl p-aminobenzoate*.—A mixture of the nitrochlorobensthiazole (1 mol.) and ethyl p-aminobenzoate (1 mol.) was gently heated in a boiling tube over a naked flame until a violent reaction took place. The product was treated with dilute ammonia and recrystallised from alcohol, when ethyl 5-nitro-1-anilinobensthiazole 4'-carboxylate was obtained in small yellow plates, m.p.  $242$ – $43^\circ$ . (Found: S, 9.5.  $C_{17}H_{13}O_4N_3S$  requires S, 9.2 per cent).

*The action of bromine on s-p-carbethoxyphenyl-p-nitrophenylthiocarbamide, and the isolation of ethyl 4'-nitro-1-anilinobensthiazole-5-carboxylate. s-p-Carbethoxyphenyl-p-nitrophenylthiocarbamide*.—A solution of p-nitroaniline (1.7 g) in alcohol (10 c.c.) was added to a solution of p-carbethoxyphenylthiocarbimide in the same solvent (2 g. in 10 c.c.) and the mixture was concentrated on a steam-bath. On recrystallisation from alcohol, the carbethoxyphenylnitrophenylthiocarbamide was obtained in orange crystals, m.p.  $154$ – $55^\circ$ , yield, 1.2 g. (Found: S, 8.9.  $C_{17}H_{15}O_4N_3S$  requires S, 9.2 per cent). In a similar experiment in which benzene was used as a medium of condensation in place of alcohol, this yield was raised to 1.8 g.

The nitrophenylthiocarbamide (0.5 g.) in chloroform (12 c.c.) was treated with bromine (1 c.c. in 1 c.c. of the same solvent) and the

mixture was heated on a steam-bath under reflux for 55 minutes. The bromo-addition compound was dried in a vacuum and reduced by sulphurous acid. On basification with ammonia ( $d$  0.880) and recrystallisation from alcohol, ethyl 4'-nitro-1-anilinobenzthiazole 4'-carboxylate was obtained in yellow crystals of a slightly deeper shade of colour than the isomeric ethyl 5-nitro-1-anilinobenzthiazole-4'-carboxylate, m.p. 241-43°. (Found: S, 9.5.  $C_{17}H_{13}O_4N_3S$  requires S, 9.2 per cent). The appearance of the two nitroanilinobenzthiazoles was quite distinct and a mixture of the two bases melted at 218°.

*The interaction of p-nitrophenylthiocarbimide and phosphorus pentachloride.*—An intimate mixture (3 g.) of *p*-nitrophenylthiocarbimide (Dyson and George, *J. Chem. Soc.*, 1924, 128, 1702) and phosphorus pentachloride (3.5 g.) was heated in a sealed tube at 150-160° for 6 hours. The dark brown oily liquid was gradually added to water to decompose phosphorus halides and the mixture was extracted with chloroform. After removal of the chloroform on a steam-bath and recrystallisation from alcohol, a yellow-brown crystalline substance was obtained, m.p. 180°. This product, however, did not possess any of the properties of 5-nitro-1-chlorobenzthiazole and admixture with a specimen of the nitro derivative obtained from 1-chlorobenzthiazole caused a depression in melting point of 40 to 50°.



## A Simple Method for the Determination of Cholesterol in Blood.

BY HIRENDRANATH BANERJI.

Quite recently much importance has been attested to the changes in the cholesterol content of blood in lipid nephrosis, diabetes and chronic obstructive jaundice, especially in relation to carbohydrate metabolism. For the estimation of cholesterol in blood common methods used are those of Bloor (*J. Biol. Chem.*, 1916, **24**, 227), Meyers and Wardell (*ibid.*, 1918, **36**, 147) and Leiboff (*J. Lab. Clin. Med.*, 1930, **15**, 776).

The method of Bloor and that of Meyers and Wardell require 1 c.c. of blood which can not be obtained without veni-puncture. In the technique of Meyers and Wardell for the determination of cholesterol, a loss of cholesterol occurs in the processes of breaking small lumps of plaster of Paris with glass rod, transference of the same from the porcelain crucible to an extraction thimble and removal of extraction flask to measuring vessel.

In Leiboff's method the apparatus used can not be easily improvised in a laboratory and moreover, the apparatus is cumbrous and costly.

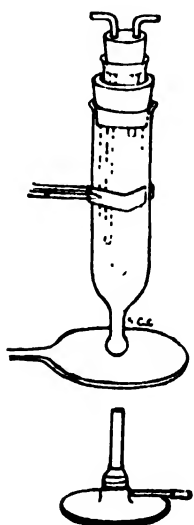


FIG. 1.

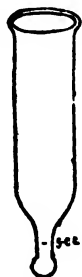


FIG. 2.



FIG. 3.

**Apparatus.**—The extraction apparatus used in this method is represented in Fig 1. It consists of a test tube (25 × 150 mm.), the lower end of which is drawn out to form a bulb of about 4 c.c. capacity with a 5 c.c. calibration mark etched on the neck of the bulb (Fig. 2). A condenser consisting of a test tube (13 × 120 mm.) fitted with a two hole stopper, through one of which is passed a long glass tube reaching to the bottom of the test tube while through the other a short glass tube is fitted. The closed rounded end of the test tube is drawn out into a tapering one as in Fig. 3 for the quick dropping of the condensed vapour. This condenser is held in place, on top of the extraction tube (Fig. 2) by a rubber stopper. The long glass tube is connected next with a water tap for flow of water.

• **Method.**—Oxalated blood (0.25 c. c.) is drained out from a pipette on a fat-free porous filter paper (Whatman filter paper no. 40 treated with alcohol and acetone) in the form of a rectangle (15 × 80 mm.) roughly. It is hung up in an incubator at 37° and dried. The portion of the filter paper containing the blood is cut into 8 or 10 pieces, untouched by hand, and placed carefully one above the other in the dry extraction tube. The pieces should be such that they do not pass through the narrow stem of the extraction tube. About 3 c.c. of redistilled chloroform are introduced into the tube. The condenser is then placed in and extraction carried on for 2 hours over a plate heated by a micro-burner or an electric hot plate, cold water being allowed to flow through the condenser during the period. The chloroform extract is cooled. At the end of the process the extraction tube is detached from the condenser. Filter paper pieces are then taken out by means of a long glass rod, bent at one end. Volume is made up to 5 c.c. mark with chloroform. In a test tube 5 c.c. of a 8 mg. % solution of cholesterol in redistilled chloroform are taken, acetic anhydride (2 c. c.) and pure concentrated sulphuric acid (0.1 c. c.) are added to the contents of each tube. The tubes are then fitted with rubber stoppers and gently tilted and rotated to get uniform mixing of the contents. Then they are allowed to stand for 15 minutes in a large beaker containing water in the light by which the colour is to be matched. The readings are then taken by colorimeter.

**Calculation.**— $\frac{S}{R} \times 0.4 \times \frac{100}{0.25} = \text{mg. of cholesterol in 100 c.c. of blood}$ , where S = reading of standard and R = reading of the unknown.



The unknown is set at 16 mm. and the result is given by 10 times the reading of the standard.

A series of parallel determinations of cholesterol in blood was carried out by the method of Meyers and Wardell (*loc. cit.*) and by the author's technique. The results are given in Table I with additional parallel determination of a known amount of cholesterol in Table II. The difference is as high as 13.8 mg. and as low as 7.7 mg. per 100 c.c. (Table II). Results are expressed in mg. per 100 c.c. of blood.

TABLE I.

Sample—whole blood.

Meyers and Wardell's.	Author's	Diff.	Meyers and Wardell's.	Author's.	Diff.
158.1	164.0	+ 5.9	156.3	176.8	+ 20.5
152.0	176.1	+ 24.1	152.0	174.7	+ 22.7
156.3	178.1	+ 21.8	170.8	177.5	+ 7.3
160.2	154.9	- 5.3	168.0	178.3	+ 10.3
153.0	168.8	+ 15.8	146.2	170.1	+ 24.1
158.0	176.0	+ 8.0	192.0	199.7	+ 7.7
180.1	181.5	+ 1.4	186.2	188.4	+ 2.2
182.5	174.2	- 8.3			

TABLE II.

Standard cholesterol solution used.

Theoretical.	Meyers and Wardell's.	Author's	Difference	
			Meyers and Wardell's	Author's
95.0	79.8	94.7	10.2	0.3
120.0	112.3	118.9	7.7	1.1
150.0	141.4	149.8	8.6	0.2
160.0	146.2	160.0	13.8	0.0
180.0	169.1	179.7	10.9	0.3
200.0	191.5	199.8	8.5	0.2

## SUMMARY.

1. A method has been described which is much simpler than that of Leiboff and more accurate than that of Meyers and Wardell.
2. Apparatus is very simple and can be easily improved in any laboratory.
3. It requires small amount of blood.
4. The loss due to transference has been completely avoided.
5. A number of estimations can be carried out simultaneously by connecting the condensers in series.
6. Remarkable economy in the use of reagents has been effected.

I am extremely grateful to Dr. R. K. Pal, M. B., D. Sc., M. R. C. P., Professor of Physiology, Prince of Wales Medical College, Patna, for guidance and direction.

DEPARTMENT OF PHYSIOLOGY  
AND BIOCHEMISTRY,  
P.W. MEDICAL COLLEGE, PATNA

*Received September 5, 1933.*

## **Sir P. C. Rây Seventieth Birthday Commemoration Medal.**

This medal will be awarded from the Indian Chemical Society by Prof. Dr. S. S. Bhatnagar, to young Indian Chemist below thirty years of age for the best single original contribution published in the Journal of the Indian Chemical Society.

### **Rules.**

1. In commemoration of the Seventieth Birthday of Sir P. C. Rây a silver medal, awarded by Prof. S. S. Bhatnagar, shall be called "Sir Prafulla Chandra Rây 70th Birthday Medal."

2. The medal on one face shall bear the profile impression of Sir P. C. Rây, and on the other face— 'Sir P. C. Rây 70th Birthday Commemoration Medal awarded to.....'"

3 The value of the medal will be Rs. 50.

4. The medal will be awarded annually for the best original paper (single and not joint) on any subject in Chemistry published in the Journal of the Indian Chemical Society only.

5. The competition for the medal shall be open to candidates whose age must not exceed thirty.

6. The candidates for the prize shall be required to submit an age certificate or corroboration of the same, confirmed by the Head of the department where they have worked.

7. The candidates, when communicating for publication in the Society's Journal, the paper intended for competition, must clearly make a statement to that effect.

8. The candidates for the medal shall submit their application not later than 31st October in every year, stating the title of their papers and the issue of the Journal in which they have been published.

9. No paper, which was submitted or has already been submitted for any other prizes or any examination, other than the M.A., or M.Sc., examination of the Indian Universities will be accepted for the present competition.

10. The merits of the papers shall be judged either by the Council of the Society or by the Board of Examiners, appointed by it, whose decision shall be considered final.

11. If in any year no prize is awarded by reason of no candidate having shown sufficient merit to entitle him to the prize or for any causes, the income of that year may be utilised in awarding a second prize in the next or in any subsequent year.

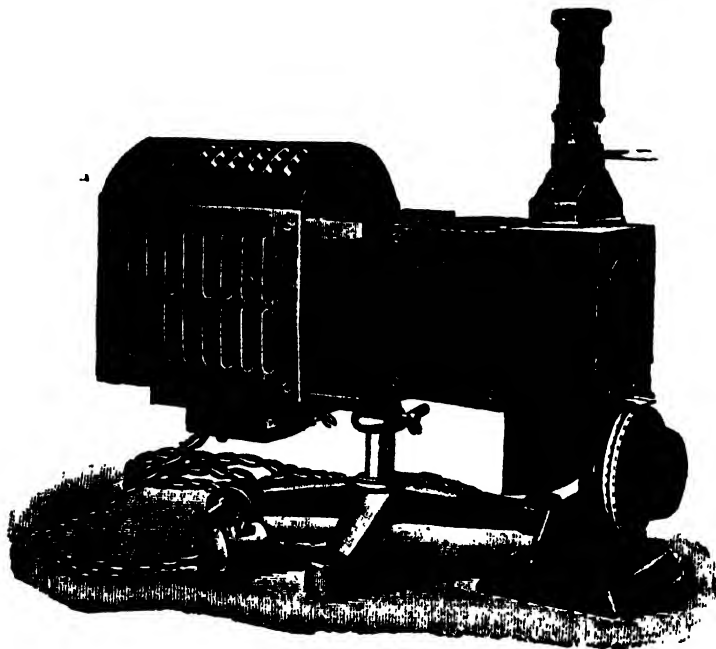
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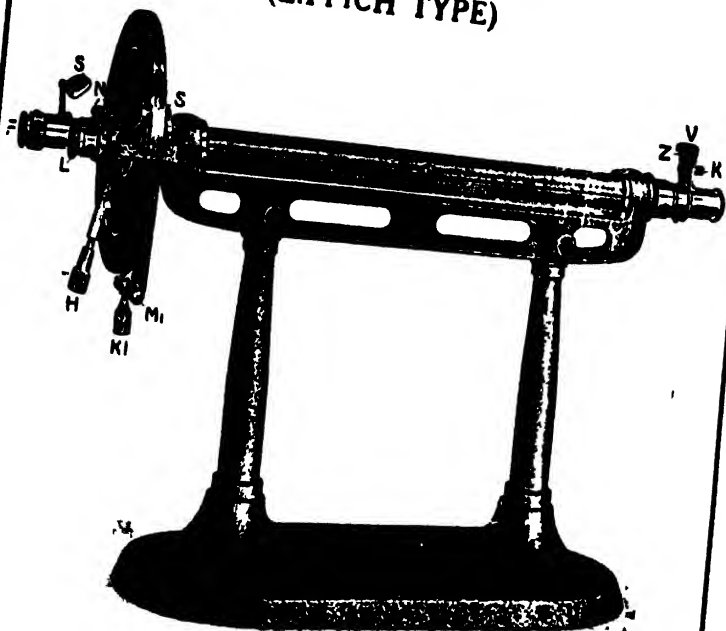


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## Constitution of the Colouring Matter of *Lawsonia Alba* Lam., or Indian Mehedi.

BY JAGARAJ BEHARI LAL AND SIKHIBHUSHAN DUTT.

*Lawsonia alba* (N. O. Lythraceae) or Mehedi as it is known in Bengali and Hindi and Henna in English is an ornamental garden shrub or hedge plant of purely Indian origin, but which has for some time been cultivated in Persia, Arabia, Mesopotamia, Egypt, Northern Africa and Southern Europe for the sake of the colouring matter contained in the leaves, which is very much prized in these countries as a dye for the hair, fingers and nails. From the point of view of Indian medicine, practically every part of the plant has found some application or other, and is used all over the country in disorders of the liver and spleen, urinary calculi, leprosy and other obstinate types of skin diseases.

But probably the most important constituent of the plant is the colouring matter contained in the leaves, which can be easily extracted by maceration with water or dilute alkali. In the state of these solutions the colouring matter has a most powerful affinity for the skin and hair and dyes an exceedingly fast shade.

There is absolutely no record of any work done on the constitution of the active principle of Indian lawsonia, although as early as 1863, Herraory (*Journal de Pharmacy*, 1863, Jan.) working on the European variety, isolated from it a tannin, which he named hennotannic acid. It was a brown resin answering in all its chemical properties to ordinary tannin. Later on Thomson (*Arch. Pharm.*, 1878, 21, 2, 483) showed that the colouring matter obtained in this way was soluble in glycerin, in ammonia, in solutions of soda and potash and in dilute acids. More recently Tommasi (*Gazzetta*, 1920, 50, 263) working on the European variety of *Lawsonia* isolated from it a crystalline colouring matter melting at 192-95° (decomp.), which he named *Lawsons* on account of its ketonic nature and which he found to possess the formula  $C_{10}H_6O_3$ . He also prepared the calcium salt, the acetyl derivative and the reduced acetyl derivative of the colouring matter.

The above represents the work that has been done on the European variety of *Lawsonia*, the Indian variety of the plant having remained practically untouched up to this time. On account of the great importance of the plant from the Indian medical point of view,

it was thought advisable by the present authors to take it under examination.

The colouring matter was prepared from the fresh leaves in a perfectly pure condition by an elaborate process including several crystallisations from benzene and acetone. It was thereby obtained in cauliflower like clusters of needles with a dark mahogany colour and metallic reflex, which when crushed in a mortar became reduced to a lemon yellow powder. It melted sharp at  $190^{\circ}$  (decomp.) and the melting point did not rise even on repeated crystallisations from various solvents. Analytical data and a number of molecular weight determinations established the molecular formula as  $C_{10}H_6O_3$ , and the preparation of monoacetyl and monobenzoyl derivatives, mono- and dioximes, phenylhydrazone, etc., showed that the substance contains phenolic hydroxy and two ketonic groups. These, together with the fact that on distillation with zinc dust it became practically quantitatively converted into naphthalene and that it possesses a persistent quinone like odour reminding of  $\alpha$ -naphthoquinone, the conclusion was almost irresistible that it must be a hydroxy- $\alpha$ -naphthoquinone. The position of the hydroxy group must be in the same nucleus which contains the quinone grouping, since on oxidation with potassium permanganate it gave rise to only phthalic acid and nothing else. Hence the only possible constitution of the colouring matter, which has also been named *lawsone* by the present authors, is that it must be 2-hydroxy- $\alpha$ -naphthoquinone. And this has been confirmed by a direct comparison of lawsone and its derivatives with synthetically prepared 2-hydroxy- $\alpha$ -naphthoquinone and the corresponding derivatives prepared from the same substance as the following table will show:

Prepared from the plant.	M.p.	Synthetically prepared	M.p.	Mixed m.p.
Lawsone	$190^{\circ}$	2-Hydroxy- $\alpha$ -N*	$190^{\circ}$	$190^{\circ}$
Acetyl lawsone	$128-29^{\circ}$	2-Acetoxy- $\alpha$ -N	$128-30^{\circ}$	$129^{\circ}$
Anilinolawsone	$190^{\circ}$	2-Anilino- $\alpha$ -N	$190^{\circ}$	$190^{\circ}$
Triacetyldihydro-lawsone	$134.5^{\circ}$	1:2:4-Triacetoxy-naphthalene	$134.5^{\circ}$	$134^{\circ}$
Lawsone phenylhydrazone	$229^{\circ}$	Benzeneazo-naphthresorcin	$229^{\circ}$	$230^{\circ}$
Lawsone mono-oxime	$180^{\circ}$	2-Hydroxy- $\alpha$ -N-oxime	$180^{\circ}$	$180^{\circ}$
Monobromolawsone	$198^{\circ}$	2-Hydroxy-3-bromo- $\alpha$ -N.	$198.5^{\circ}$	$198^{\circ}$
Lawsone ethylether	$126.97^{\circ}$	2-Hydroxy- $\alpha$ -N-ethylether	$126^{\circ}$	$126^{\circ}$

\* N = naphthoquinone.

By a glance at the above table and comparing it with the work done by Tommasi (*loc. cit.*) it becomes quite evident that the compound he obtained from European *Lawsonia* was in all probability identical with the lawsone obtained by the present authors from Indian *Lawsonia* in spite of small difference in the melting point as reported by him. In other words the Indian and the European varieties of *Lawsonia* probably contain the same colouring matter lawsone, which is identical with 2-hydroxy- $\alpha$ -naphthoquinone.

#### EXPERIMENTAL.

*Isolation of lawsone.*—Five kilos of the fresh leaves were crushed in a stone mortar (iron should not be used) and extracted with a 5% solution of sodium bicarbonate, three times in succession for a period of 24 hours each, in large enamelled iron basin. After the third extraction the leaves were practically devoid of colour and the combined extracts were acidified with strong sulphuric acid diluted with an equal volume of water. The resultant voluminous precipitate which consisted of the crude colouring matter was filtered off and dried and a further small quantity was obtained by saturating the filtrate with common salt and filtering again. The crude substance was then extracted with dilute ammonium hydroxide, filtered and the filtrate precipitated with concentrated hydrochloric acid and the process repeated twice. Finally the precipitate after drying, was extracted with benzene and the solvent distilled off when the colouring matter was obtained in the form of orange-yellow crusts, melting at 185-88°. It was then dissolved in sodium carbonate solution, filtered and the orange-yellow filtrate precipitated with concentrated hydrochloric acid. The precipitate was filtered, washed with distilled water until free from chloride, dried and repeatedly crystallised from benzene and acetone until the melting point went up to 190° and did not rise any further. The substance thus isolated has a dark mahogany-bronze colour in the crystalline and a lemon-yellow colour in the powdered state, yield 2.5 g. or .05% of the weight of the fresh leaves.

The substance is very sparingly soluble in cold water with an orange-yellow colour and the solution undergoes decomposition on boiling. It is slightly soluble in chloroform, bromoform, acetic acid, benzene and petroleum ether and moderately soluble in alcohol, benzene and ether. The solution in all these solvents has a bright orange-yellow colour. It is very easily soluble in solutions of alkali

carbonates, bicarbonates and hydroxides, forming orange-red solutions which quickly undergo decomposition when boiled. In the cold the colouring matter can be reprecipitated unchanged from the above solutions by treatment with dilute acids. The substance is fairly acidic in reaction and produces a brisk evolution of carbon dioxide from sodium bicarbonate although not from sodium carbonate. It is also feebly acidic to litmus paper in aqueous or aqueous alcoholic solution. Alcoholic solution of the substance gives an immediate orange precipitate with alcoholic lead acetate, but does not give any precipitate with either alcoholic silver nitrate, copper acetate, nickel acetate, ferric chloride or calcium chloride, although a deep red colour is developed with nickel acetate and a reddish brown colour with ferric chloride. (Found: C, 69.18, 69.12, 69.01; H, 3.51, 3.52, 3.47; M. W. 170, 177, 178. (b. p. method in acetone); 172, 175 (silver salt); 176.5, 175.5 (lead salt).  $C_{10}H_6O_3$  requires C, 68.9; H, 3.4 per cent. and M. W. 174).

*Silver salt.*—To an alcoholic solution of lawsone (1 g.) neutralised by the addition of a few drops of dilute ammonia, alcoholic silver nitrate was added until the red precipitate was no longer formed. This was filtered off, washed and dried. Red amorphous substance resembling cinnabar in appearance. (Found: C, 42.82; H, 1.81; Ag, 88.67, 88.39.  $C_{10}H_5O_3Ag$  requires C, 42.71; H, 1.78; Ag, 88.44 per cent).

*Ammonium salt* was obtained by dissolving lawsone (1 g.) in the smallest quantity of concentrated ammonia and allowing the solution to evaporate completely at the ordinary temperature. Bright red crystalline substance, exceedingly soluble in water and alcohol and decomposing between 150-70° without melting. (Found: C, 63.55; H, 5.59.  $C_{10}H_5O_3N$  requires C, 62.83; H, 5.98 per cent).

*Neutral lead salt.*—To an aqueous solution of the ammonium salt prepared as above, aqueous lead acetate was added when an amorphous yellow precipitate was obtained. This was filtered, washed and dried. (Found: C, 43.00; H, 2.02; Pb, 87.14.  $C_{20}H_{10}O_6Pb$  requires C, 43.32; H, 1.80; Pb, 87.55 per cent).

*Lead acetate double salt.*—To an alcoholic solution of lawsone, alcoholic lead acetate was added drop by drop, until the precipitate was no longer formed. This was filtered off, washed with alcohol and dried. Bright orange glistening plates, slightly soluble in water and alcohol. (Found: C, 82.77; H, 2.04; Pb, 47.6.  $C_{10}H_5O_3 \cdot Pb \cdot COCH_3$  requires C, 82.73; H, 1.82; Pb, 47.28 per cent).

*Sodium salt* was prepared by adding a concentrated solution of sodium hydroxide to a solution of lawsone in dilute sodium hydroxide. The glistening red crystalline precipitate was filtered through asbestos and dried in the vacuum desiccator. It could not however be obtained in a sufficiently pure state for analysis.

*Acetyl lawsone* was prepared from lawsone and acetic anhydride in the usual manner. It crystallised from alcohol in pale yellow plates, m.p. 128-29°. (Found: C, 66.43; H, 3.98.  $C_{10}H_5O_3 \cdot COCH_3$  requires C, 66.66; H, 3.79 per cent).

*Triacetyldihydrolawsone*.—Lawsone (2 g.) was boiled with acetic anhydride (10 g.) under reflux and moist zinc dust gradually added until the solution was completely decolourised. The mixture was then filtered into cold water and stirred and the resulting white precipitate filtered off and crystallised from dilute alcohol in lustrous white laminæ, m.p. 134.5°. (Found: C, 63.38; H, 4.72.  $C_{16}H_{14}O_6$  requires C, 63.45; H, 4.68 per cent).

*Anilinolawsone*.—A mixture of lawsone (2 g.), aniline (4 g.) and glacial acetic acid (8 g.) was heated under reflux for 3 hours and then poured into water. The resulting dark red precipitate was filtered off and crystallised from alcohol in long scarlet needles, m.p. 190°. (Found: C, 76.89; H, 4.55.  $C_{16}H_{11}O_2N$  requires C, 77.10; H, 4.41 per cent).

*Lawsone mono-oxime* was prepared from lawsone (1 mol.) and hydroxylamine acetate (1 mol.) in the usual manner. It crystallised from alcohol in bright yellow needles, m.p. 180°. It dissolves in alkalis and organic solvents with a bright yellow colour. It is a powerful dyestuff. (Found: C, 68.35; H, 3.87.  $C_{10}H_6O_2 \cdot NOH$  requires C, 68.49; H, 3.70 per cent).

*Lawsone dioxime* was obtained by treating lawsone with a slightly more than the theoretical quantity of hydroxylamine. The substance crystallised from alcohol in light yellow glistening needles, m.p. 200° (decomp.). (Found: N, 13.75.  $C_{10}H_6O_3N_2$  requires N, 13.46 per cent).

*Lawsone phenylhydrazone*.—A mixture of lawsone (0.8 g.), phenylhydrazine (0.5 g.) and alcohol (2 c.c.) was allowed to stand at the ordinary temperature for 12 hours and then cautiously diluted with water. The phenylhydrazone separated in scarlet-red prisms which were crystallised from alcohol, m.p. 229° (decomp.). (Found: N, 10.57.  $C_{16}H_{12}O_2N_2$  requires N, 10.76 per cent).

*Lawsone ethyl ether*.—A mixture of the silver salt of lawsone (4 g.) and ethyl bromide (2 g.) was heated in a pressure flask on the

water-bath for 4 hours. After cooling the bottle was opened, the excess of ethyl bromide evaporated off and the residue extracted with alcohol and the filtered extract allowed to stand when the ethyl ether crystallised out in glistening yellow needles, m.p. 126-27°.

*Monobromolawsone.*—Lawsone (1 g.) dissolved in warm acetic acid was treated with an acetic acid solution of bromine, until it was no longer decolourised even on boiling. On cooling, the bromo derivative crystallised out in yellow prisms which were recrystallised from alcohol, m.p. 198°. (Found : Br, 32.2.  $C_{10}H_5O_3Br$  requires Br, 31.6 per cent).

*Distillation of lawsone with zinc dust.*—Lawsone, on distillation with zinc dust in a current of hydrogen in the usual manner, gave an almost quantitative yield of naphthalene.

*Oxidation of lawsone with alkaline potassium permanganate.*—Lawsone (5 g.) dissolved in dilute sodium hydroxide was treated with a 3 % aqueous solution of potassium permanganate until the latter was no longer decolourised. The precipitated manganese dioxide was filtered off, the filtrate evaporated to a small volume and acidified with dilute hydrochloric acid, when masses of colourless needles (m.p. 213°) gradually separated which were identified to be phthalic acid. No other product could be detected.

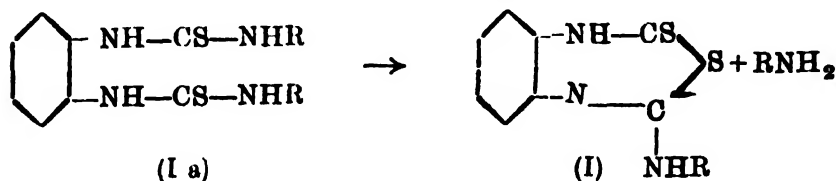
*Benzeneazolawsone.*—Aniline was diazotised and coupled with lawsone dissolved in excess of dilute sodium hydroxide. A red precipitate, insoluble in water or alkalis was produced, which was filtered off, washed with dilute hydrochloric acid and water and finally crystallised from alcohol in scarlet needles melting above 305°. The substance could not be obtained in sufficient quantity for complete examination.



# The Influence of Attached Rings on the Formation of Heterocyclic Compounds. Part I.

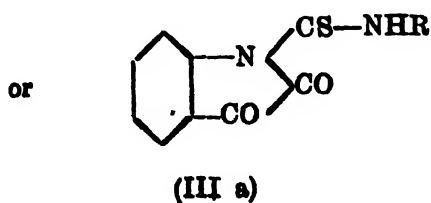
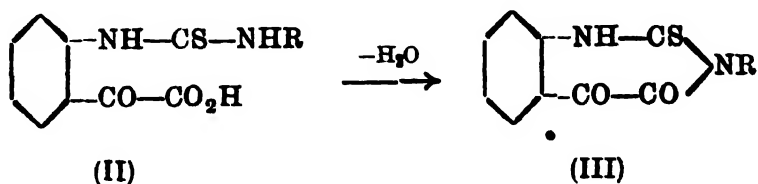
BY TEJENDRA NATH GHOSH.

It has been shown in a previous communication (*J. Indian Chem. Soc.*, 1929, 6, 181) that strong hydrochloric acid converts *o*-phenylenediaminedithiocarbamides into heptathiodiazine derivatives.



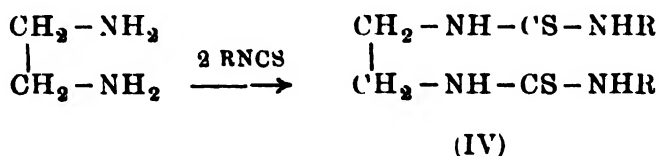
In continuation of the same work, some new substituted thiocarbamide derivatives have been prepared with the object of making a comparative study of the ease and nature of their transformation into cyclic structures as conditioned by the presence of one or more phenylene residues.

*o*-Thiocarbamidobenzoylformic acids (II), prepared by the action of thiocarbamides on *o*-aminobenzoylformic acid gives heptadiazine derivatives (III) on treatment with acetic anhydride.

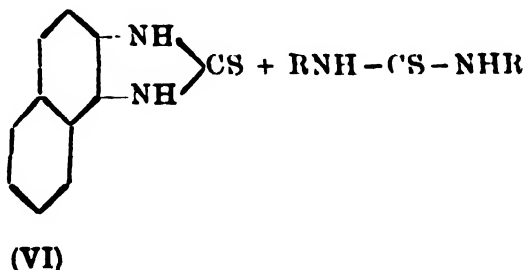
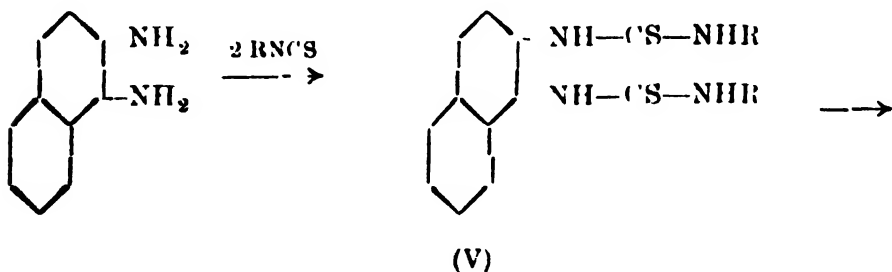


The alternative formula (III a) has been rejected on the ground that the compound does not suffer any change on being boiled with acetic anhydride or strong hydrochloric acid, though in accordance with the observation of De (*J. Indian Chem. Soc.*, 1926, 3, 82) a compound of this structure (III a) would have lost the thiocarbamido group. It is soluble in cold dilute alkali and is precipitated unchanged by acids and forms an insoluble lead salt.

Ethylenediaryldithiocarbamides (IV), prepared by the action of two molecules of mustard oil on ethylenediamine remain unchanged even when boiled with strong hydrochloric acid or 15 % caustic potash solution.

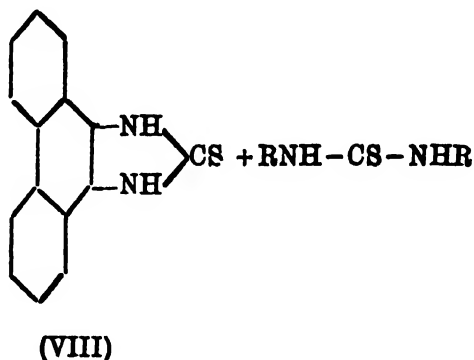
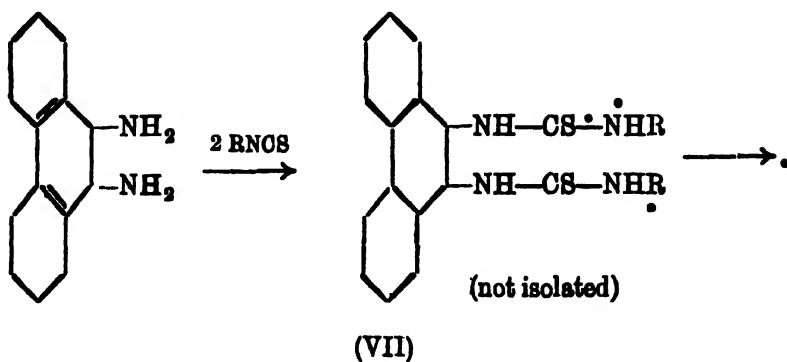


1:2-Naphthylenediaryldithiocarbamides (V) in contrast with the ethylenedithiocarbamides, suffer ring-closure readily on being treated with strong hydrochloric acid or 15 % caustic potash solution to yield naphthylenethiocarbamide (VI).



The tendency of the phenanthrene-9:10-dithiocarbamides for ring-closure is so very great that during the process of their formation

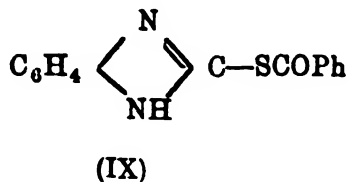
from 9:10-diaminophenanthrene and mustard oils, they actually pass into the cyclic thiocarbamide (VIII).



That the solvent pyridine does not exert any ring-closing influence in this reaction has been proved by the fact that 1:2-naphthylenediamine under similar condition yields only 1:2-naphthylenedithiocarbamide (V).

A comparison of the above reactions shows clearly how the phenylene residue plays a very important part in the formation of cyclic structures. Ethylenedithiocarbamide in which there is no phenylene residue, does not give any ring compound; compounds (I a) and (II) contain one phenylene residue and they give heptathiodiazine and heptadiazine derivatives respectively. Naphthylenedithiocarbamide derivative (V) containing two phenylene residues gives the most stable cyclic thiocarbamide. The presence of one more phenylene residue in phenanthrene-9:10-dithiocarbamide (VII) is so very helpful for ring-closure that it cannot even be isolated. The tendency to ring-closure, thus, appears to increase with the increase in the number of phenylene residues.

The cyclic thiocarbamides (VI, VIII) are similar to *o*-phenylene-thiocarbamide prepared by Lellmann (*Annalen*, 1884, 221, 14) in all their properties. *o*-Phenylenethiocarbamide yields only one alkali-insoluble monobenzoyl derivative (IX) though *o*-phenylenecarbamide has been found by Heller and collaborators (*J. pr. Chem.*, 1925, ii, 111, 1) to yield, under varying conditions of experiment, two different benzoyl derivatives *viz.*, *N-N'*-dibenzoyl and mono-oxybenzoyl. It is clear, therefore, that *o*-phenylenethiocarbamide can exist only in the monothiol form.



#### EXPERIMENTAL.

*o*-Phenylthiocarbamidobenzoylformic acid (II, R=Ph).—Phenyl-mustard oil (2·7 g.) was added to an alcoholic solution of the potassium salt of *o*-aminobenzoylformic acid (4 g.) prepared according to the method of Erdmann (*J. pr. Chem.*, 1841, 24, 13) and the solution was boiled under reflux for about 2 hours, cooled and then acidified with dilute hydrochloric acid when a white solid separated which crystallised from alcohol in colourless rectangular plates, m.p. 173-74° (decomp.), yield 4 g. It is soluble in sodium bicarbonate solution. (Found: N, 9·21.  $\text{C}_{15}\text{H}_{12}\text{O}_3\text{N}_2\text{S}$  requires N, 9·38 per cent).

1-*N*-Phenyl-2-thioketo-4:5-benzo-6:7-diketo-1:3-heptadiazine (III, R=Ph).—The above compound (II, R=Ph) was heated under reflux with excess of acetic anhydride for about an hour. The clear solution was diluted with water and evaporated almost to dryness, when a tarry mass was obtained which was treated with a dilute solution of caustic soda. The alkaline solution on acidification gave a solid which crystallised from acetone in colourless rectangular plates, m.p. 155-57°. It is insoluble in sodium bicarbonate solution. (Found: N, 9·71; S, 11·68.  $\text{C}_{15}\text{H}_{10}\text{O}_2\text{N}_2\text{S}$  requires N, 9·92; S, 11·84 per cent).

*oo*-Tolylthiocarbamidobenzoylformic acid (II, R=*o*-tolyl).—The method of preparation was the same as in the case of the preceding compound (II, R=Ph). It crystallised from alcohol in colourless

rectangular plates, m.p. 208-10° (decomp.). (Found: N, 8.59.  $C_{16}H_{14}O_3N_2S$  requires N, 8.91 per cent).

1-N-o-Tolyl-2-thioketo-4:5-benzo-6:7-diketo-1:3-heptadiazine (III, R=o-tolyl).— The method of preparation was the same as in the case of the preceding compound (III, R=Ph). It crystallised from acetone in colourless rectangular plates, m.p. 205-06°. (Found: S, 11.12.  $C_{16}H_{12}O_2N_2S$  requires S, 10.81 per cent).

op-Tolylthiocarbamidobenzoylformic acid (II, R=p-tolyl) crystallised from alcohol in colourless rectangular plates, m.p. 165-66° (decomp.). (Found: N, 8.64.  $C_{16}H_{14}O_3N_2S$  requires N, 8.91 per cent).

o-Phenylcarbamidobenzoylformic acid.—Phenyl isocyanate (2.4 g.) was added to an alcoholic solution of potassium salt of o-aminobenzoylformic acid (4 g.) and the solution was boiled under reflux for about an hour, cooled and then acidified with dilute hydrochloric acid when a white solid came out, the bicarbonate solution of which yielded on acidification a white solid which crystallised from alcohol in beautiful colourless prisms, m.p. 170-80°, yield 4 g. (Found: N, 9.71.  $C_{15}H_{12}O_4N_2$  requires N, 9.85 per cent). The compound, on treatment with acetic anhydride yielded a tarry product which could not be purified.

Ethylene-sym-diphenyldithiocarbamide (IV, R=Ph) was prepared according to the method of Lellmann and Würthner (*Annalen*, 1885, 228, 234); the action of strong hydrochloric acid or 15 % caustic potash solution did not produce any change upon this and other ethylenedithiocarbamides.

Ethylene-sym-di-p-tolyldithiocarbamide (IV, R=p-tolyl).— The method of preparation was the same as in the case of the preceding compound, yield almost quantitative. The compound crystallised from alcohol in colourless prisms, m.p. 104-95°. (Found: N, 15.62.  $C_{18}H_{22}N_4S_2$  requires N, 15.64 per cent).

Ethylene-sym-di-o-tolyldithiocarbamide (IV, R=o-tolyl) crystallised from alcohol in colourless prisms, m.p. 180°. (Found: N, 15.69.  $C_{18}H_{22}N_4S_2$  requires N, 15.64 per cent).

Ethylene-sym-diallyldithiocarbamide (IV, R=allyl) crystallised from alcohol in colourless prisms, m.p. 103-04°. (Found: N, 21.68.  $C_{10}H_{18}N_4S_2$  requires N, 21.70 per cent).

Ethylene-sym-dimethyldithiocarbamide (IV, R=Me).— The method of preparation was the same as before, m.p. 85-86°. (Found: N, 27.85.  $C_6H_{14}N_4S_2$  requires N, 27.18 per cent).

**1:2-Naphthylenethiocarbamide (VI).**—1:2-Naphthylenediphenyldithiocarbamide (6·7 g.) prepared according to the method of Schieffelin (*Ber.*, 1889, 22, 1877), was heated under reflux on the water-bath with 15% caustic potash solution (140 c.c.) for 10 hours. The filtered solution, on acidification with dilute hydrochloric acid, yielded a white solid which was dried and carefully weighed, yield 20·5%. It crystallised from pyridine in colourless plates, m.p. above 800°. It is soluble in cold dilute alkali and precipitated by acids. It forms an insoluble lead salt. Like *o*-phenylenethiocarbamide it also cannot be desulphurised by yellow oxide of mercury. (Found: N, 14·41; S, 16·14.  $C_{11}H_8N_2S$  requires N, 14·0; S, 16·0 per cent). The same compound (VI) was obtained when 1:2-naphthylenediphenyldithiocarbamide was heated with strong hydrochloric acid under reflux for about an hour.

*o*-Phenylenediphenyldithiocarbamide (6·7 g.) was similarly heated on the water-bath with 15% caustic potash solution (140 c.c.) for 10 hours. The yield of the thioheptadiazine (I, R=Ph) was 19·5%.

**1:2-Naphthylenedi-*p*-tolylthiocarbamide (V, R=*p*-tolyl).**—An alcoholic solution of 1:2-naphthylenediamine (1·6 g.) was heated under reflux on the water-bath with *p*-tolylmustard oil (8 g.) for about an hour when a white crystalline precipitate was obtained which crystallised from alcohol in colourless prisms, m.p. above 800°, yield 3·6 g. (Found: N, 12·01.  $C_{26}H_{24}N_4S_2$  requires N, 12·28 per cent). Like the corresponding phenyl compound (V, R=Ph) it also gave 1:2-naphthylenethiocarbamide (VI) when heated with 15% caustic potash solution or strong hydrochloric acid.

**1:2-Naphthylenedixylyldithiocarbamide (V, R=xylyl).**—The method of preparation was the same as in the case of the preceding compound (V, R=*p*-tolyl), m.p. above 800°. The xylylmustard oil used here has been obtained from 1:3:4-xylidine. (Found: N, 11·31.  $C_{28}H_{28}N_4S_2$  requires N, 11·57 per cent). It also gave 1:2-naphthylenethiocarbamide with 15% caustic potash solution.

**9:10-Phenanthrenethiocarbamide (VIII).**—A pyridine solution of 9:10-diaminophenanthrene hydrochloride (2·8 g.), freshly prepared according to the method of Pschoor (*Ber.*, 1902, 35, 2788; Schmidt, *Ber.*, 1908, 41, 3684), was heated under reflux with phenylmustard oil (2·7 g.) and the requisite amount of sodium acetate dissolved

in the smallest quantity of water, for about  $\frac{1}{2}$  an hour when a crystalline precipitate was obtained which crystallised from pyridine in brownish rectangular plates, m.p. above  $800^{\circ}$ . It is soluble in cold dilute alkali and precipitated by acids. It gives an insoluble lead salt with lead acetate solution, yield 1.6 g. (Found: N, 11.17; S, 18.14.  $C_{15}H_{10}N_2S$  requires N, 11.20; S, 18.80 per cent). From the mother liquor diphenylthiocarbamide was isolated and identified with a genuine sample.

The same compound (VIII) was obtained when a pyridine solution of 9:10-phenanthrenediamine hydrochloride was heated with *p*-tolyl- or *o*-tolylmustard oil.

1-Benzoylthiol-8:4-benzo-2:5-diazole (IX).—The benzoyl derivative was prepared by the usual method and crystallised from alcohol in colourless plates, m.p.  $186-87^{\circ}$ . (Found: S, 12.34.  $C_{14}H_{10}ON_2S$  requires S, 12.59 per cent). *o*-Phenylenethiocarbamide was dissolved in various proportions of alkali, but in each case the monosodium salt was obtained which yielded the above monobenzoyl derivative (IX).

My thanks are due to Prof. P. C. Guha, D. Sc. for his keen interest in the present investigation.





## Halogenation. Part V. Bromination and Iodination of some Fatty Acids.

By PHULDEO SAHAY VARMA AND V. T. SHRIDHARA MENON.

Bromo derivatives of the fatty acids are generally obtained either by the direct action of bromine in presence of halogen carriers at high temperatures, sometimes under pressure, or by the replacement of hydroxyl group in the hydroxy derivatives of the fatty acids by the action of hydrobromic acid or phosphorus bromide. Iodo derivatives are obtained either by the action of phosphorus iodide on the hydroxy derivatives of the fatty acids or by the replacement of bromine in the bromo derivatives of the acids by means of iodine.

Attempts have been made in this paper to prepare the bromo and iodo derivatives of some of the fatty acids with the help of potassium bromide and sulphuric acid and iodine and sulphuric acid respectively. In the case of lower fatty acids poor yield of the halogen derivatives has been obtained, whereas in the case of higher fatty acids comparatively a much better yield of the  $\alpha$ -bromo and  $\alpha$ -iodo derivatives has been found. No appreciable difference in the yield of iodoacetic acid is noticeable when acetic acid or acetic anhydride is used for the purpose. A slightly better yield of the bromo and iodo derivatives is obtained with acetic acid or acetic anhydride when nitrosulphonic acid mixture (a mixture containing about 50% of fuming nitric acid and about 50% of nitrosulphonic acid, the latter obtained by passing a current of dry sulphur dioxide through nitric acid) is used in place of concentrated sulphuric acid. In other cases, there is no appreciable difference in the yield of the halogen derivatives, when concentrated sulphuric acid or nitrosulphonic acid mixture is employed.  $\alpha$ -Bromo derivatives have been obtained from acetic acid, acetic anhydride, propionic acid, butyric anhydride, *iso*-butyric acid, lauric acid, myristic acid, palmitic and stearic acids and  $\alpha$ -iodo derivatives from acetic acid, acetic anhydride, propionic acid,  $\alpha$ -butyric anhydride, *isobutyric* acid, palmitic and stearic acids.

### EXPERIMENTAL.

The acid or the anhydride was taken in a flask provided with a reflux condenser, potassium bromide or iodine (as the case may be)

was added and the flask heated on a water-bath. Concentrated sulphuric acid or nitrosulphonic acid (as the case may be) was then added ( $\frac{1}{2}$  c.c. at a time). Heating was continued for about 5 hours and then the mixture treated with sulphurous acid to remove any excess of bromine or iodine and then extracted with ether. The ethereal solution was dried with calcium chloride and ether evaporated off on a water-bath. If the residue left behind is solid, it is purified by crystallisation from water or alcohol. If the residue is liquid, it is distilled under reduced pressure. The results obtained with different acids or anhydrides are summarised in the following table.

Substance.	Amount taken.	Halogenating agent.	Product.
Acetic acid	20 c.c.	Potassium bromide (5g.) and nitrosulphonic acid mixture (10 c.c.)	Bromoacetic acid (1 g.), m.p. 49-50°
Acetic anhydride	"	"	"
Propionic acid	"	Potassium bromide (5g.) and conc. sulphuric acid (10 c.c.)	$\alpha$ -Bromopropionic acid (3 g.), b.p. 204-207°
Butyric anhydride	"	"	$\alpha$ -Bromobutyric acid (5 g.), b.p. 127°/25 mm.
isoButyric acid	"	"	$\alpha$ -Bromoisobutyric acid (5 g.), m.p. 48°
*Lauric acid	5 g.	"	$\alpha$ -Bromolauric acid (2.5 g.), m.p. 31.5°
*Palmitic acid	"	"	$\alpha$ -Bromopalmitic acid (3 g.), m.p. 52°
*Stearic acid	"	"	$\alpha$ -Bromostearic acid (3 g.), m.p. 60°
Acetic acid	20 c.c.	Iodine (5 g.) and nitrosulphonic acid mixture (10 c.c.)	Iodoacetic acid (1 g.), m.p. 83°
Acetic anhydride	"	"	"
Propionic acid	"	"	$\alpha$ -Iodopropionic acid (1 g.), m.p. 45°
Butyric anhydride	"	"	$\alpha$ -Iodobutyric acid (4.5 g.), m.p. 41°
isoButyric acid	"	"	$\alpha$ -Iodoisobutyric acid (4.5 g.), m.p. 73.5°
*Palmitic acid	5 g.	"	$\alpha$ -Iodopalmitic acid (2 g.), m.p. 57°
*Stearic acid	"	"	$\alpha$ -Iodostearic acid (2 g.), m.p. 66°

\* Carbon tetrachloride (10 c.c.) used as solvent.

## Halogenation. Part VI. Bromination and Iodination of Benzonitrile.

BY PHULDEO SAHAY VARMA AND NIRODE BARAN SEN-GUPTA.

Bromo and iodo derivatives of benzonitrile have been obtained before by indirect methods only either from the corresponding aniline derivatives by the replacement of amino group by cyanogen or from the corresponding benzoic acid derivatives by the replacement of carboxyl group by cyanogen group. It is reported that the action of bromine on benzonitrile under ordinary conditions results in the formation of benzonitrile monobromide and dibromide, whereas in a sealed tube at 200°-360° it results in the formation of perbromo-benzonitrile (Engler, *Annalen*, 1865, 133, 144; 1867, 142, 74; Friedburg, *ibid.*, 1871, 158, 29). Bromine or iodine alone, or in presence of other substances such as nitric or sulphuric acids, does not yield any bromo or iodo derivatives of benzonitrile, but the bromo and iodo derivatives have now been obtained by the action of potassium bromide or potassium iodide and concentrated sulphuric acid on benzonitrile.

### EXPERIMENTAL.

*Action of potassium bromide and sulphuric acid on benzonitrile.*—Strong sulphuric acid (5 c.c.) was taken in a test tube and benzonitrile (10 c.c.) was carefully poured into it over the heavy layer of sulphuric acid, care being taken not to allow the acid to mix freely with benzonitrile. Potassium bromide (4 g.) was then slid down the side of the test tube when bromine was set free by the action of sulphuric acid and reacted with benzonitrile which turned gradually into a solid product. At the end of 3 hours the upper solid layer was removed and treated with a small quantity of cold water, shaken and filtered. On evaporating the filtrate to dryness and recrystallising the solid product from cold water, a white crystalline substance (2.5 g.), melting at 112°, was obtained. It was found to be *p*-bromobenzonitrile. (Found: N, 7.48; Br, 48.66.  $C_6H_4BrCN$  requires N, 7.7; Br, 48.97 per cent). The residue was digested with water at

50° and filtered. The filtrate was concentrated and allowed to cool, when needle-shaped crystals (0.6 g.), melting at 52°, were obtained. It was found to be *o*-bromobenzonitrile. (Found: Br, 48.72.  $C_6H_4BrCN$  requires Br, 48.97 per cent).

The solid residue still left behind was boiled with water and filtered. The filtrate was evaporated to dryness and crystallised from boiling water. The product (0.8 g.) so obtained, m. p. 121°, was found to be benzoic acid. The last portion of the residue was digested with alcohol and crystallised from it, m. p. 128° and was found to be benzamide (0.4 g.). (Found: N, 11.59.  $C_7H_7ON$  requires N, 11.57 per cent).

*Action of potassium iodide and sulphuric acid on benzonitrile.*—Benzonitrile (10 c. c.) was treated with strong sulphuric acid (5 c.c.) and potassium iodide (4 g.) exactly in the same way as in the preceding experiment. Benzonitrile layer was kept cold by pouring cold water over it under the tap. It solidified, the solid was removed after 3 hours and treated successively with cold water, water at 50°, boiling water and finally with alcohol. Solid crystalline products were obtained from these solvents. *p*-Iodobenzonitrile (2 g.). (Found: N, 6.28. I, 55.12;  $C_6H_4ICN$  requires N, 6.1; I, 55.46 per cent). *o*-Iodobenzonitrile (0.7 g.) (Found: I, 54.83.  $C_6H_4ICN$  requires I, 55.46 per cent). Benzoic acid (0.7 g.) and benzamide (1.1 g.) were also obtained.

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## Halogenation. Part VII. Iodination and Bromination of Naphthalene and $\beta$ -Naphthol.

BY PHULDEO SAHAY VARMA, D. N. MOZUMDAR AND  
K. KUNJAN RAJAH.

Iodonaphthalene is not ordinarily obtained by direct iodination and the yield obtained by the methods already known is very poor. Noelting (*Ber.*, 1886, 19, 135) obtained this compound by digesting  $\alpha$ -naphthalene diazonium sulphate with potassium iodide in an acid solution. Otto and Mörtes (*Annalen*, 1868, 147, 173) obtained iodonaphthalene by the action of iodine on a solution of mercuri-di- $\alpha$ -naphthyl in carbon disulphide. Edinger and Goldberg (*Ber.*, 1900, 33, 2882) prepared this compound along with  $\beta$ -iodonaphthalene by the action of sulphur iodide and excess of nitric acid on naphthalene in light petroleum at 100° for several hours. Datta and Chatterji (*J. Amer. Chem. Soc.*, 1917, 39, 485) obtained a mixture of iodo- and mononitronaphthalenes by the action of iodine in presence of concentrated nitric acid.

Attempts have been made in these experiments to iodinate naphthalene under different conditions and the best yield is obtained by iodinating in presence of a mixture of nitrosulphonic acid and fuming nitric acid.

Iodo- $\beta$ -naphthol has been obtained by Meldola (*J. Chem. Soc.*, 1885, 47, 525) by adding iodine to an acetic acid solution of  $\beta$ -naphthol, sodium acetate and lead acetate. Lepetit (*Gazette*, 1890, 20, 107) seems to have obtained this compound by the action of nitrogen iodide on  $\beta$ -naphthol dissolved in caustic soda. Monoiodo derivative of  $\beta$ -naphthol has now been obtained by iodinating  $\beta$ -naphthol in presence of a number of reagents, but the best yield is obtained in presence of ammonium hydroxide. The nascent nitrogen iodide formed by the action of iodine on ammonium hydroxide seems to be the active iodinating agent in this case.

Naphthalene is more readily brominated and if bromination is carried on in presence of substances like mixture of fuming nitric and nitrosulphonic acids, not only a very good yield of the bromo derivatives is obtained, but there is also no evolution of hydrobromic

acid at all, thus avoiding the wastage of bromine in the form of hydrobromic acid.

$\beta$ -Naphthol has been directly brominated before and a number of bromo derivatives have been obtained (Smith, *J. Chem. Soc.*, 1879, 35, 789; Armstrong, *Chem. News*, 1889, 59, 225; 1891, 63, 186; Felensa, *Ber.*, 1894, 17, 1480). The best yield of the bromo derivatives is, however, obtained when bromination is carried on at low temperatures, preferably at 10°, in presence of a third substance such as concentrated or fuming sulphuric acid.

#### EXPERIMENTAL.

*Iodination of naphthalene.*—Naphthalene, iodine and glacial acetic acid were heated in a flask on a sand-bath, provided with a reflux condenser. Nitrosulphonic acid mixture (equal quantities of fuming nitric acid and nitrosulphonic acid) was then dropped little at a time from the top of the condenser. When the whole of the acid mixture was added, the contents of the flask were heated for some specified period, at the end of which they were boiled with animal charcoal (1–2 g.), filtered and concentrated to a smaller volume. The liquid obtained was then distilled under reduced pressure on a paraffin bath. Iodine and acetic acid were then distilled off and the residue containing the iodo derivative was extracted with benzene and the benzene distilled off. A liquid boiling at 302–303° was thus obtained. It gave naphthalene when boiled with alcoholic potash and formed golden yellow needles of picrate, m.p. 127°. It is therefore  $\alpha$ -iodonaphthalene.

In a few cases, it has been found equally convenient to pour the whole of the reaction product into a large quantity of water when the heavy layer of the iodo compound settles at the bottom. It is then separated in a tap funnel, washed several times with 10% potassium hydroxide, then with water, dried by means of anhydrous calcium chloride and distilled. The experiments are given in Table I.

TABLE I.

Naphthalene = 10 g.

Iodine.	The third substance used.	Reaction period.	Yield of iodo-naphthalene.
5 g.	Potassium persulphate (5 g.)	3 hr.	3.2 g.
5	Chromic acid (5 g.)	1½	3.4
6	{ Fuming sulphuric acid (5 c.c.) { Fuming nitric acid (5 c.c.)	3	4.0

TABLE I (contd.).

Iodine.	The third substance used.	Reaction period.	Yield of iodo-naphthalene.
6 g.	Strong nitric acid (5 c.c.)	2½ hr.	3·6 g.
6	Fuming nitric acid (5 c.c.)	2½	3·7
6	Nitrosulphonic acid mixture (5 c.c.)	2½	4·2
10	Nitrosulphonic acid mixture (15 c.c.)	1½	6·2
	Glacial acetic acid (10 c.c.)		

*Iodination of  $\beta$ -naphthol.*—A better yield of iodo- $\beta$ -naphthol than what was obtained by Meldola (*loc. cit.*) was obtained by iodinating  $\beta$ -naphthol by means of iodine dissolved in KI solution in presence of ammonia. For this purpose,  $\beta$ -naphthol (5 g.) was dissolved in concentrated ammonia (10 c.c.) and iodine (4·5 g.) in KI solution was then added drop by drop and shaken. When the whole of the iodine solution was added, the product was poured into dilute sulphuric acid when a flocculent white precipitate was obtained. This crystallised from acetic acid, m.p. 93-94°, yield 9·2 g.

*Bromination of Naphthalene.*—Naphthalene (10 g.) dissolved in carbon tetrachloride, was refluxed on a water-bath. Bromine (2 c.c.) dissolved in the same solvent was then added drop by drop. When the whole of the bromine was added, the third substance (if any) was then dropped little at a time and the whole of these operations took about an hour. The contents of the flask were then heated on a sand-bath to drive off the solvent, the residue extracted with dilute alcohol. On standing, the extract separated into two layers. The lower layer was separated, washed with dilute alcohol, dehydrated over calcium chloride and distilled. The fraction distilling at 283°-285° was found to be monobromo derivative.

If the product contains a nitro derivative also, the nitro derivative separates out in a crystalline form from the alcoholic extract and is separated and purified. The results are summarised in Table II.

*Bromination of  $\beta$ -naphthol.*— $\beta$ -Naphthol (5 g.), dissolved in acetic acid (20 c.c.), was put into a flask, immersed in a thermostat at 10° and bromine (1·8 c.c.) dissolved in acetic acid (15 c.c.) was added to it drop by drop from a tap funnel and the flask was shaken after each addition. When the whole of the bromine solution was added the flask was allowed to stand for about an hour in the thermostat and then the contents poured into a porcelain dish and allowed

to stand for about 12 hours, when long light-brown needles separated out. By repeated crystallisation from acetic acid or from petroleum ether in which the bromo compounds are soluble, fine shining crystals of 1-bromo- $\beta$ -naphthol (m.p. 88-84°) or of 1:6-dibromo- $\beta$ -naphthol (m.p. 105-06°) were obtained. The results are summarised in Table III with 5 g. of  $\beta$ -naphthol, the time allowed for the reaction being 1½ hours in each case, in the last case bromine added being 3.6 c.c.

TABLE II.

Third substance used.	Yield of monobromo naphthalene.
...	3.4 g. (21%)
Aluminium-mercury couple (2 g.)	4.5 g. (28%)
Strong nitric acid (5 c.c.)	4.5 g. (36%)
Fuming nitric acid (5 c.c.)	7.6 g. (47%) also mono-nitro-naphthalene (2 g.)
Nitro sulphonic acid mixture (5 c.c.)	10.1 g. (62%) also mono-nitronaphthalene (3 g.)

TABLE III.

Third substance used.	Yield.
Diffused sunlight	1-Bromo- $\beta$ -naphthol (5.6 g.)
Strong sulphuric acid (1 c.c.)	1-Bromo- $\beta$ -naphthol (5.8 g.)
Fuming sulphuric acid (1 c.c.)	1-Bromo- $\beta$ -naphthol (6.5 g.)
Aluminium-mercury couple (1.5 g.)	1-bromo- $\beta$ -naphthol (3.8 g.)
Fuming sulphuric acid. (1 c.c.)	1:6 Dibromo- $\beta$ -naphthol (3.5 g.)



## Studies in the Coagulation of Colloids. Part VI. Further Investigation of the Viscosity Variations during Coagulation.

By SHRIDHAR SARVOTTAM JOSHI and T. MADHAB MENON.

In Part V of this series (*J. Indian Chem. Soc.*, 1933, 10, 329) results were given for the changes of viscosity during the slow coagulations of colloid arsenious sulphide (both pure and also when protected by different amounts of gelatine) produced by differently concentrated solutions of potassium chloride. It was observed that (a) immediately after the commencement of the coagulation the viscosity almost always showed a *diminution* in the range, 0.7 to 1.8 % of the initial viscosity, and that (b) the viscosity—time curves showed a number of well marked maxima and minima which were attributed to the coagulation process (at any rate in the *slow* region) consisting of a succession of changes, both as to the size and nature of the coagulating particles (*vide infra*). In view of the fact that both these findings invalidate the use of viscosity as a *general*, qualitative measure of the degree of coagulation at least in the *slow* region, and especially since the initial fall in viscosity mentioned in (a) does not appear to have been studied previously in the literature, it was considered desirable to investigate (a) and (b) in more detail. To this end, in the following experiments coagulations of the arsenious sulphide sol have been studied in which differently concentrated solutions of  $\text{AlCl}_3$ ,  $\text{Th}(\text{NO}_3)_4$ ,  $\text{ThCl}_4$ , KF, KCl, KBr, and KI were used as coagulants, the sol being also varied over a suitable range in each case.

### EXPERIMENTAL.

• The general experimental procedure was mostly similar to that described in Part V (*loc. cit.*). The temperature of the thermostat was maintained at  $35 \pm 0.1^\circ$  in all the experiments. The colloid content of the sol was determined by the Kessler's method (*cf.* Part I, *J. Indian Chem. Soc.*, 1931, 8, 11). 20 C. c. of the sol

were kept in the Scarpa tube (called P in Fig. A, Part V) immersed in the thermostat. To this was added an equal volume of the coagulator solution whose concentration was varied by mixing appropriate volumes of water of the standard solution of the electrolyte chosen. Both these were allowed to attain the thermostat temperature before mixing in the Scarpa tube. Immediately after this, the mixture was given a rotatory motion twice and the corresponding mean time noted. The viscosity of the coagulating sol was then determined by Scarpa's method with modifications described in Part V. By preliminary experiments the concentrations of the electrolyte solution and of the sol were so chosen, that the coagulating sol did not flocculate, that is, show heterogeneities of even fine visible precipitate tending to leave a deposit on the walls of the viscometer in at least 5 hours.

It has been noted previously (*loc. cit.*) that the initial fall of viscosity occurs so soon after the start of coagulation that precautions are necessary to measure it fully and accurately. Some improvement over the previously adopted procedure was made in these experiments (for details compare a forthcoming paper by Joshi and Joga Rao on the viscosity variations due to molecular chemical changes) by dispensing with the letting out of water from the aspirator  $A_1$  into the beaker B (*cf.* Fig. A, Part V) in order to establish negative pressure in the Scarpa tube before each observation of the time of rise of the liquid. Following this rise, the water level in the manometer limb connected with the tube P is slightly depressed. This is easily adjusted to the original value by simply adding a small quantity of water to that in the beaker B. This results in a considerable saving of time, and what is more, is particularly suited for measurements during the initial stages of the coagulation. The suction used in these experiments was 26 cm. of water.

Curves 1-4, in Fig. 1 show the influence of varying the sol concentration in the range 1.5 to 0.188 g.  $As_2S_3$  per litre, the concentration of the coagulant being kept constant at  $N/40,000$ . Curves 5-6 refer to coagulations of sols of a fixed colloid content (1.5 g.  $As_2S_3$  per litre) and the coagulant concentrations varied in the range  $N/20,000$  to  $N/27,000$ . Figs. 2 and 3 refer to similar experiments with thorium nitrate and thorium chloride solutions. Results of the use of solutions of the various potassium halide solutions are given in Figs. 4 and 5. The data recorded in Tables

I—V were obtained from curves in the corresponding figures. The colloid and the electrolyte concentrations given in the third and fourth vertical columns in these tables refer to their values in the coagulating mixture.

TABLE I (cf. Fig. 1).

Sol = 20 c.c.

Composition of the mixture.	Colloid conc. $\text{As}_2\text{S}_3$ g./litre.	Electrolyte conc.	Initial viscosity in centipoise.	First minimum viscosity in C.P. $\eta_M$ .	Percentage diminution of viscosity.	Time corresponding to $\eta_M$ in mins.
Water. N/1000 $\text{AlCl}_3$ .						
19 c.c. 1 c.c.	1.5	N/40000	0.728	—	—	—
" "	0.75	"	0.734	0.729	0.64	25
" "	0.375	"	0.733	0.728	0.64	25
" "	0.188	"	0.735	"	"	25
18.5 1.5	1.5	N/26270	0.735	0.732	0.39	27
18.35 1.65	"	N/24250	0.727	0.723	0.52	21
18.15 1.75	"	N/22880	0.731	0.727	0.46	27
18.15 1.85	"	N/21620	0.751	0.739	0.3	19
18 2	"	N/20000	0.742	0.740	0.23	19

TABLE II (cf. Fig. 2).

Sol = 20 c.c.

Water. N/500- $\text{Th}(\text{NO}_3)_4$ .						
19 1	1.5	N/120000	0.735	0.733	0.30	25
" "	0.75	"	0.729	0.727	0.27	—
" "	0.188	"	0.728	0.727	0.18	13
" " "	0.094	"	0.727	0.726	0.14	27

TABLE III (cf. Fig. 3).

Sol = 20 c.c.

Water. N/500. $\text{Th}(\text{Cl})_4$ .						
18.6 1.4 c.c.	1.5	N/14290	0.736	0.734	0.20	38
18.5 1.5	"	N/13500	0.725	—	—	—
18 2	"	N/10000	0.741	0.738	0.48	25
17.7 2.3	"	N/8500	0.730	0.724	0.70	38
17 3	"	N/6500	0.733	0.737	—	—

TABLE IV (cf. Fig. 4).

Sol = 20 c.c.

Composition of the mixture.	Colloid conc. $As_2S_3$ g./litre.	Electrolyte conc.	Initial viscosity in centipoise	First minimum viscosity in C.P. $\eta_M$ .	Percentage diminution of viscosity.	Time corresponding to $\eta_M$ in mins.	
Water. N/10-KF.							
18 c.c.	2 c.c.	1.5	N/200	0.731	0.721	1.3	60
16	4	„	N, 100	0.738	0.727	1.5	25
18	2	0.75	N/200	0.730	0.722	1.1	37
16	4	„	N/100	0.732	0.723	1.17	75
N/10-KCl.							
18	2 c.c.	1.5	N/200	0.729	0.724	0.73	37
16	4	„	N/100	0.732	0.723	1.2	25
„	4	0.75	N/100	0.724	0.722	0.36	25
18	2	„	N, 200	0.731	0.720	1.42	50

TABLE V (cf. Fig. 5).

N/10- KBr.									
16	c.c.	4	c.c.	1.5	N/100	0.729	0.722	0.85	38
18		2		„	N/200	0.734	0.727	0.98	38
18		2		0.75	N, 200	0.729	0.722	0.85	50
N/10- KI.									
16		4	c.c.	1.5	N/100	0.727	0.720	0.98	25
		4		0.75	„	0.728	0.725	0.41	25

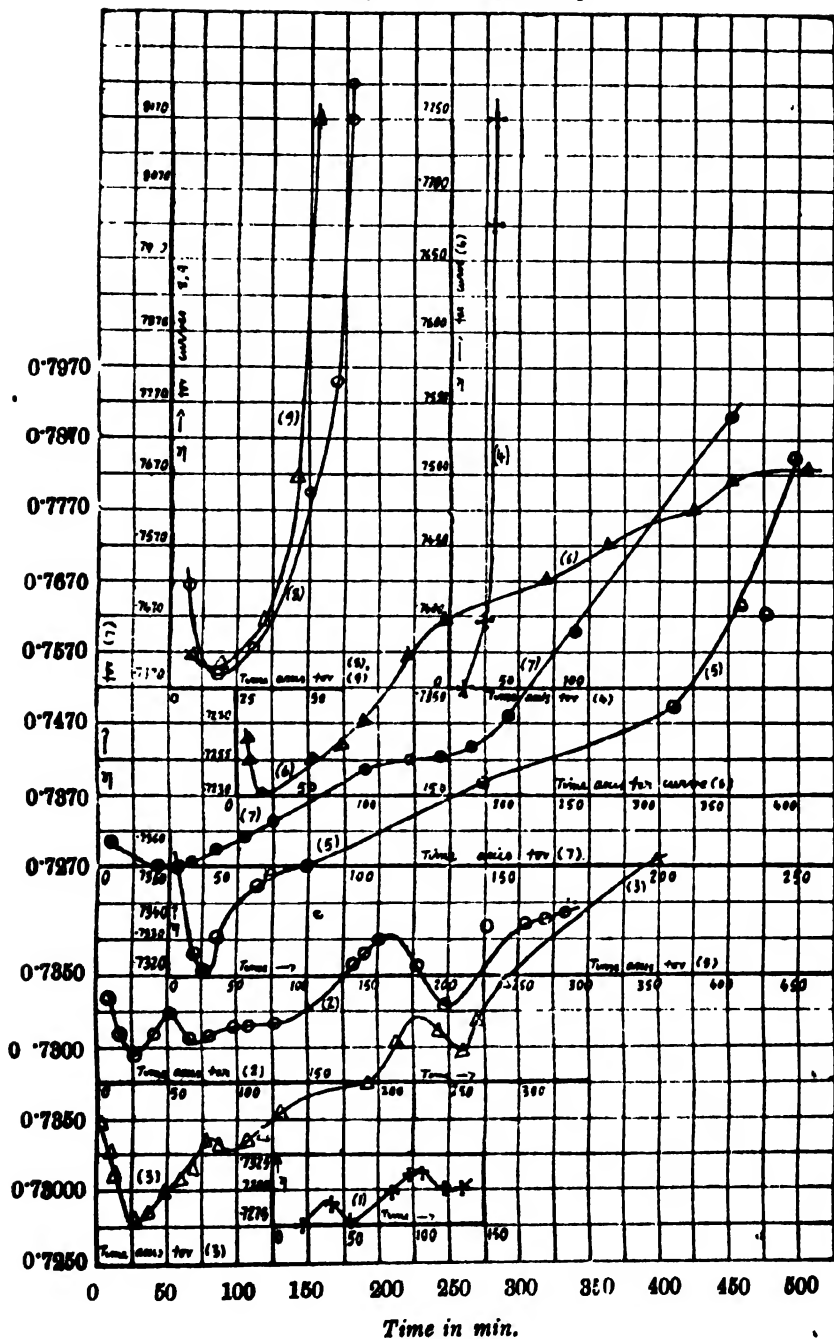
## DISCUSSION.

Amongst the numerous methods used in order to follow the progress of coagulation, the earliest and widest used depend upon the variation, of the intensity of light scattered by, and of the relative transparency of the coagulating sol (Mukherjee and coworkers, *J. Chem. Soc.*, 1920, 117, 350, 1503; 1924, 125, 794; Lottermoser, *Kolloid Z.*, 1914, 13, 145; Desai, *Trans. Faraday Soc.*, 1928, 24, 181). Hatschek's colorimetric method (cf. Anderson, *ibid.*, 1924, 19, 626) and that using the ultramicroscope are more accurate and their

results (especially of the last) simpler to interpret, but are restricted in the range of their applicability. A considerable mass of data has also resulted from the use by different workers of chemical methods of measuring coagulation (Paine, *Koll. Chem. Beih.*, 1912, 4, 24; Paine and Evans, *Trans. Faraday Soc.*, 1924, 24, 649; Freundlich and Basu, *Z. physikal. Chem.*, 1925, 115, 203; Joshi and Prabhu, *J. Indian Chem. Soc.*, 1931, 8, 11, 337). Joshi and Lal (*J. Indian Chem. Soc.*, 1933, 10, 61) have measured coagulation by a new method, viz., by the determination of the surface tension. Reference also must be made here of the results of numerous workers (for a review, cf. Part V) on viscosity measurements although restricted, in by far the majority of cases, to a determination of the significant transpiration times only. An outstanding indication of these results is that in general the progress of coagulation is continuous with the coagulation time. It is of considerable interest, therefore, to point out that the confirmation by the results recorded in this paper, of the previous observation (cf. Part V) of (a) the initial fall of viscosity, and of (b) the marked discontinuities on the viscosity-time curves affords a definite evidence of the limitation of the above deduction at least in the slow region of coagulation. These results (and those reported in Part V) also show the superiority of our viscosity method in revealing features of the coagulation process, which otherwise practically escape detection (cf. Joshi and Joga Rao, *J. Indian Chem. Soc.*, 1933, 10, 247).

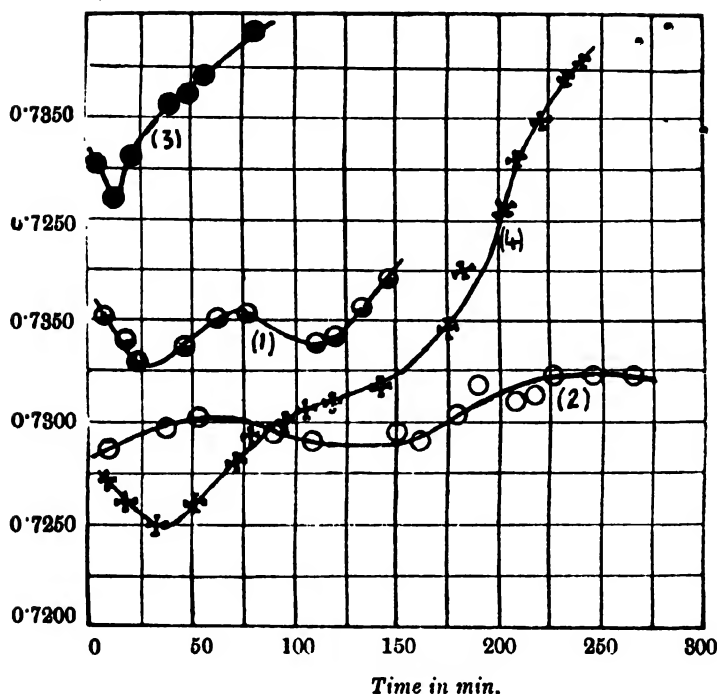
An examination of the foregoing results also shows (Figs. 1—5) that the magnitude of the initial fall, and the subsequent fluctuations of viscosity are affected considerably by the values of the concentration both of the colloid and the electrolyte. It is also seen (cf. curves 1—4, Fig. 1) that the initial fall in viscosity tends to diminish both for the smallest and largest concentrations of the sol, and of the coagulator. It is well known that the rate of coagulation increases rapidly as the coagulator concentration is raised, and ordinarily, the viscosity would rise rapidly in such coagulations. It is to be anticipated, therefore, that in these cases, the initial fall in the viscosity would be to some extent masked by the viscosity rise due to the rapidity of coagulation. It must be stressed, however, that the above deductions represent only a tentative conclusion, not quite free from exceptions (cf. Figs. 2—3), and a far more detailed investigation would be necessary to obtain a complete correlation of the progress of viscosity as a function of the two concentration

FIG. 1.  
Coagulation by  $\text{AlCl}_3$ .



Curves 1—4 refer to  $N/40,000 \text{ AlCl}_3 + 1.5 \text{ g.}, 0.75 \text{ g.}, 0.375 \text{ g.},$  and  $0.188 \text{ g. As}_2\text{S}_3$  per litre respectively. Curves 5—9 refer to  $N/26270, N/24250, N/22880, N/2102$  and  $N/20,000 \text{ AlCl}_3$  respectively  $+ 1.5 \text{ g. As}_2\text{S}_3$  per litre.

FIG. 2.

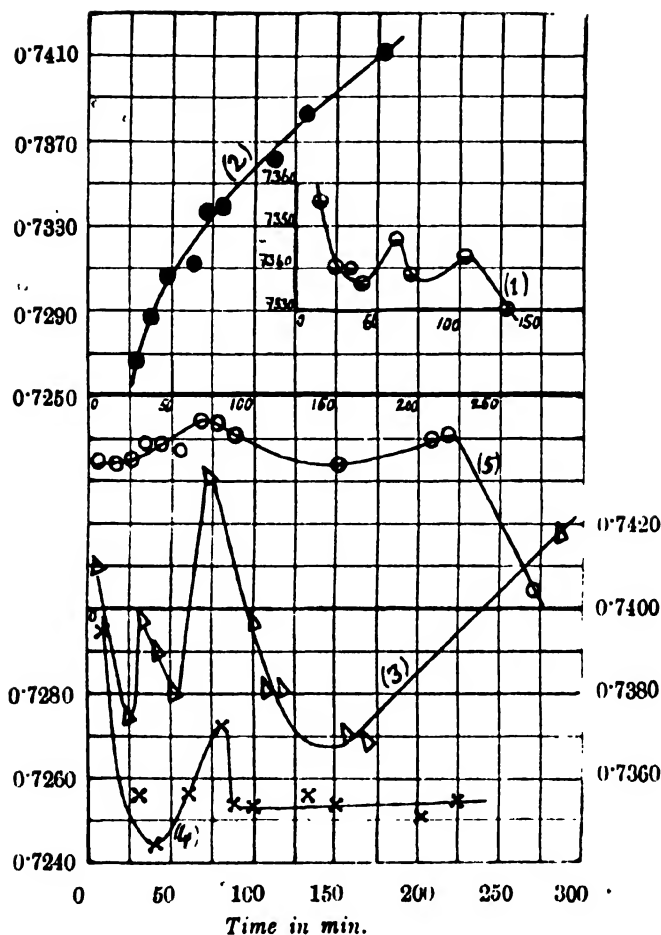
*Coagulation by  $\text{Th}(\text{NO}_3)_4$ .*

Curves 1—4 refer to  $N/20,000 \text{ Th}(\text{NO}_3)_4 + 1.5 \text{ g., } 0.75 \text{ g., } 0.188 \text{ g., and } 0.04 \text{ g. of } \text{As}_2\text{S}_3$  per litre respectively.

factors in the *slow* region. For example, curve, 1 (Fig. 3), curves 1—2 (Fig. 4), and curve 3 (Fig. 5) show that a coagulation is not necessarily accompanied by a net rise of viscosity. Results fully confirming this possibility under appropriate conditions have been obtained recently in these laboratories and will be published shortly.

It was also observed in Part V (*loc. cit.*) that subsequent to the initial fall and prior to its eventual rise, in a number of coagulations, the viscosity increased markedly slowly, indicative of *autocatalysis*. This is detectable in curves 5, 6, 7 (Fig. 1). It is well known that a small percentage change in the coagulator concentration affects the coagulation time by several times in the *slow* region. It is

FIG. 8.

Coagulation by  $\text{ThCl}_4$ .

Curves 1—5 refer to  $N/14290$ ,  $N/13500$ ,  $N/10,000$ ,  $N/8500$  and  $N/6500$   $\text{ThCl}_4$  respectively and  $1.5 \text{ g. As}_2\text{S}_3$  per litre.

interesting, therefore, to notice that the time corresponding to the attainment of the first minimum on the viscosity-time curves varies irregularly in the range 20—60 minutes although the nature and the strength of the coagulator and also of the colloid were varied over a wide range (*cf.* Tables I-V). Results obtained previously were similar to this (*loc. cit.*). It might also be added that the value of the initial fall expressed as a percentage observed previously for potassium chloride solutions is similar to that observed now for solutions of  $\text{KF}$ ,  $\text{KBr}$ , and  $\text{KI}$ .



FIG. 4.

Coagulation by KF and KCl.

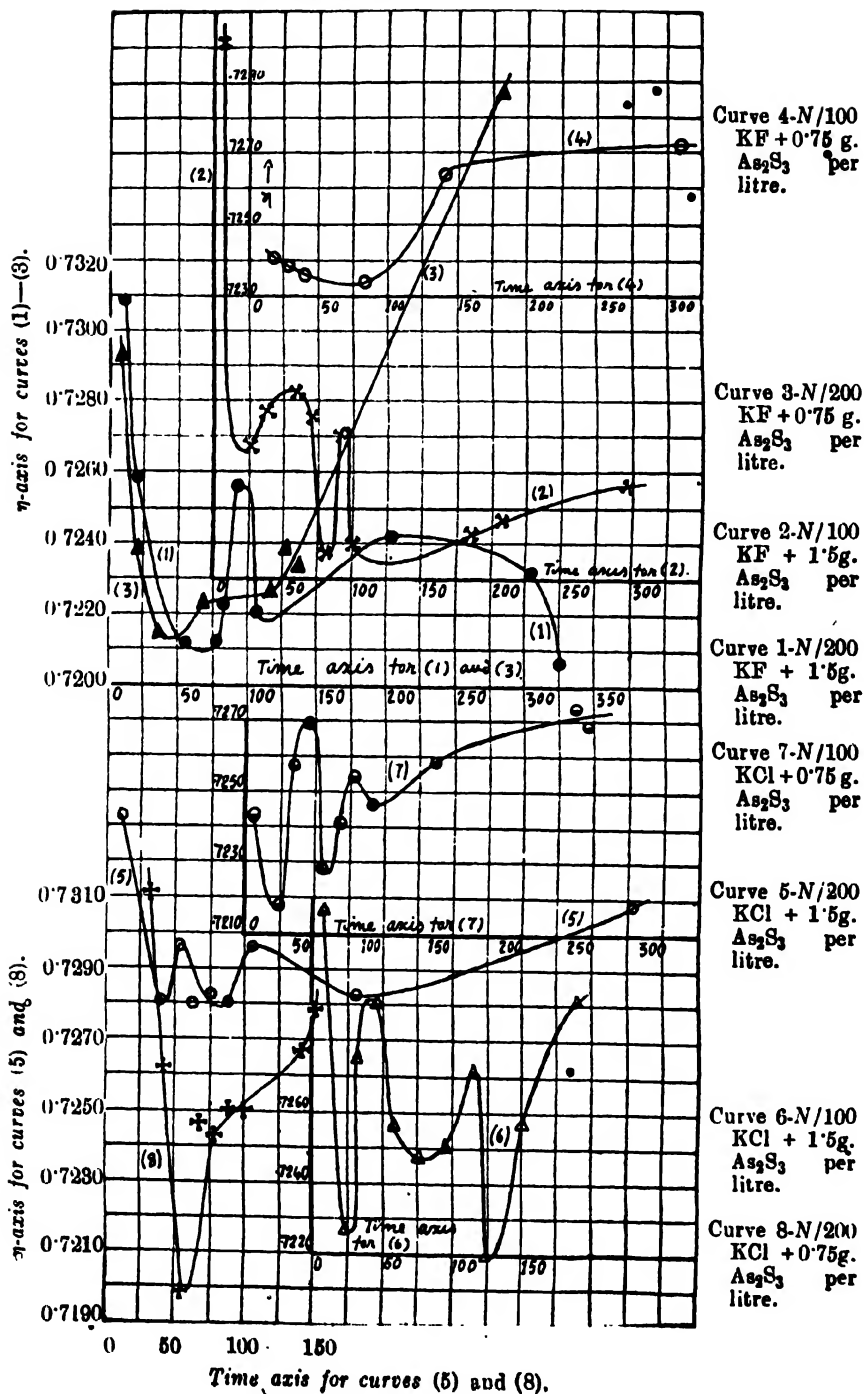
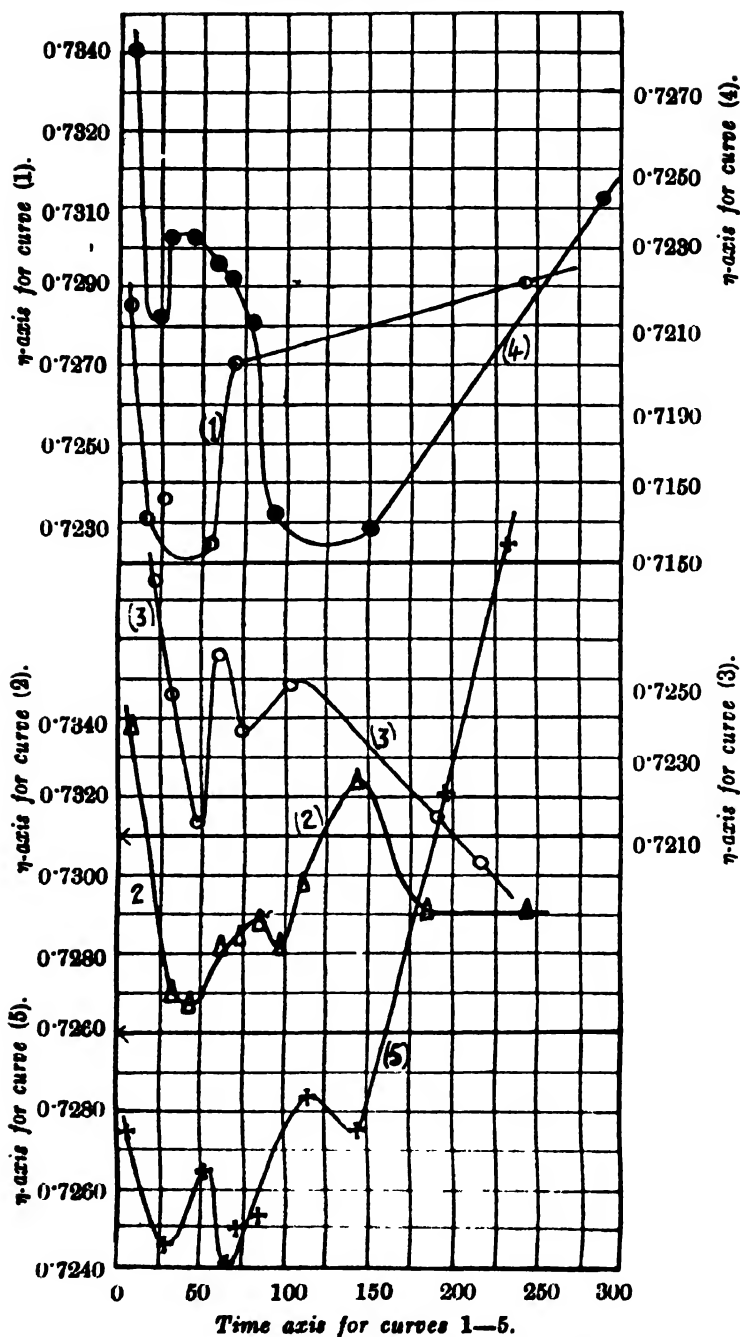


FIG. 5.  
Coagulation by KBr and KI.



Time axis for curves 1-5.  
 Curve 1- N/100 KBr + 1.5g.  $\text{As}_2\text{S}_3$  per litre.  
 2- N/200 " " " "  
 3- " " 0.75g. " "  
 4- N/100 KI + 1.5g. " "  
 5- " " 0.75g. " "

## SUMMARY.

Results are given for the variation of viscosity when differently concentrated sols of arsenious sulphide were coagulated in the slow region, by solutions of KCl, KBr, KI, KF,  $\text{AlCl}_3$ ,  $\text{ThCl}_4$ , and  $\text{Th}(\text{NO}_3)_4$ . Usually, though not invariably, viscosity first diminishes to a well marked minimum and then rises in a number of breaks. The first tends to diminish when the concentration of the sol and of the coagulator is either too high or too low. Both the above features disappear during rapid coagulations.

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## **A Convenient Micro Method of Estimating Sulphur in Organic Compounds. A Modification of ter Meulen's Method.**

BY HARISH CHANDRA GOSWAMI AND PULIN BIHARI SARKAR.

All micro methods of estimation of sulphur in organic compounds consist in oxidising the sulphur and estimating the resulting sulphuric acid either gravimetrically or volumetrically. The methods of oxidation of sulphur can be divided into three groups, (i) oxidation in the dry way (fusion method), (ii) oxidation in the wet way, and (iii) direct oxidation by means of pure oxygen.

*Oxidation by fusion method*.—Recèsei (*Chem. Ztg.* 1926, 50, 785) fused the substance with sodium carbonate and sodium peroxide and the resulting sulphate was precipitated as barium sulphate and weighed in a micro-Neubauer crucible. Emerson (*J. Amer. Chem. Soc.*, 1930 50, 1291) finds that sodium peroxide is not suitable, firstly because it does not keep well and secondly, because in certain cases oxidation takes place with explosive violence. Emerson used  $\text{KNO}_3$  in place of  $\text{Na}_2\text{O}_2$ . The fusion mixture is prepared once for all by mixing 2 parts of  $\text{Na}_2\text{CO}_3$  with 1 part of  $\text{KNO}_3$ . The method is good in case of solids but not convenient for liquids, especially when they are volatile. Complete analysis requires 3-4 hours.

*Oxidation in the wet way* (Micro-Carius method of Emich Donau, (*Monatsh.* 112, 33, 169).—It is of limited applicability. Besides the manipulative inconveniences, it is unsuitable for organic sulphides, which are oxidised to sulphones. Electrolytic oxidation in presence of  $\text{HNO}_3$  (method of Gasparini, modified by K. Heller, *Mikrochemie*, 1929, 7, 209) requires a special apparatus and a longer time (more than 5 hours).

*Direct oxidation by means of pure oxygen*.—This is the classical method of Pregl and is the most accurate method suitable for solids, liquids and gases. In this method the substance is burnt in a current of oxygen and the products of combustion are passed over red hot platinum and then over a Jena glass spiral moistened with perhydrol diluted with five times its volume of water. The sulphur is determined in the washings of the Jena glass spiral by acidifying with

hydrochloric acid and precipitating with barium chloride and weighed as barium sulphate in a micro-Neubauer crucible. In the absence of halogens and nitrogen the porcelain beads are soaked in neutral hydrogen peroxide and the resulting sulphuric acid determined volumetrically.

Later improvements of Pregl's method are concerned mainly with the complete precipitation of barium sulphate and its transference. Wintersteiner (*Mikrochemie*, 1924, 2, 14) and Eigenberger (*Z. anal. Chem.*, 1926; 68, 220) used dilute celluloid gel for rapid coagulation of barium sulphate. Heyl and Fullerton (*Chem. Zentr.*, 1923, IV, 519) used "alkalimetric titration of benzidine sulphate.

Guillemet (*Bull. Soc. chim.*, 1932, 51, 1611) recommends the precipitation of sulphuric acid as benzidine sulphate and filtering through Jena sintered glass filter tubes (No. 13f. G. 3). He claims his procedure to be more rapid than Pregl's. Though these methods are excellent they require manipulative skill of the experimenter and his previous training in micro-technics. The procedure requires 3-4 hours.

Kubota and Hanai (*Bull. Chem. Soc. Japan*, 1928, 3, 168) estimated sulphur volumetrically after converting it into  $H_2S$ . The substance is heated in hydrogen and the products passed over freshly reduced nickel heated to  $200^\circ$ . The whole of sulphur is retained as nickel sulphide. The nickel sulphide is then taken out in a flask and heated with HCl in a current of hydrogen and the sulphur estimated exactly as in the "Evolution method" in the case of steel analysis. The method is good but requires 3-4 hours.

H. ter Meulen (*Rec. trav. chim.*, 1922, 142. *Chem. weekblad.*, 1926, 348; 1930, 19) introduced a new method of catalytic hydrogenation for the estimation of sulphur in organic compounds. The compound is gasified in a current of excess of hydrogen and the mixture is passed over a catalyst (platinised asbestos or simply pure asbestos) heated to redness by means of a Fletcher furnace. The sulphur is quantitatively converted to  $H_2S$ , which is absorbed in caustic soda. The alkali solution is then treated with acidified standard  $N/20$ -iodine solution and excess of iodine titrated with  $N/20$ -thiosulphate solution. Sulphur calculated from the iodine consumed:  $H_2S + 2 I = 2 HI + S$ . H. ter Meulen took 80 mg. of the substance and used ordinary macro-burette.

1 C. c.  $N/20$ -iodine soln.  $\Omega$  0.8 mg. of S.

This method was used by the present authors for the last two years and gave excellent results.

It occurred to us that using a microburette with which 0.005 c.c. can be easily read and with  $N/100$ -iodine solution we can estimate up to 0.008 mg. of sulphur. We accordingly tried to see whether by slight modification this method which is very handy and accurate requiring barely three quarters of an hour, can be applied in micro sulphur estimation.

This method has the following advantages over Pregl's method:

(1) Troublesome precipitation and transference of barium sulphate is done away with.

(2) The micro-balance is used only for weighing the original substance.

(3) It does not require experience in micro-technics and infinite attention to details.

(4) It requires  $1/4$ th the time of Pregl's method.

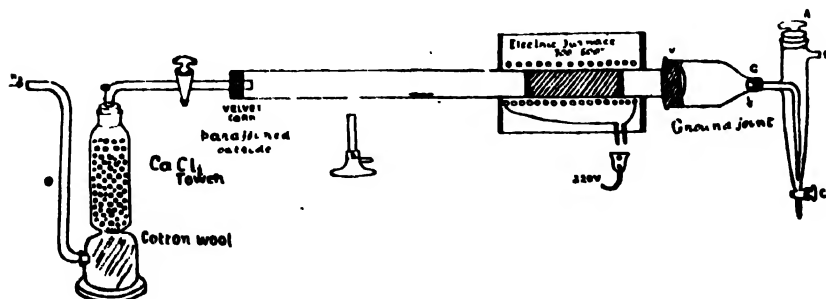
(5) Much simpler than that of Pregl without any appreciable loss in accuracy.

All weighings were done in a Kuhlmann micro-balance. In case of liquids Pregl's micro-technics of filling in a capillary were followed.

#### EXPERIMENTAL.

A diagram of the apparatus used is shown below: The apparatus consists of a quartz tube 40 cm. in length and 10 mm. in diameter. 8 Cm. of the tube length are filled with platinised asbestos which is maintained at  $700-800^{\circ}$  by means of a small electric furnace 16 cm. long. The asbestos layer is kept at a distance of 5-6 cm. from the end. The end of the quartz tube is connected by means of a sound velvet cork (V) well paraffined outside, with a larger glass tube of 20 mm. in diameter and 60 mm. in length. The other end is drawn out and fitted with a ground-joint (G) with the absorption cell. The object of the wide tube is to condense the high boiling hydrocarbons which may be formed in certain cases.

FIG. 1.



The absorption cell (A) as shown in the figure consists of a glass tube of 10 mm. in diameter drawn out and fitted with a stop-cock (C)

The capacity of the cell is approximately 5 c. c. The inlet-tube which is fitted with the ground-joint (G) of the larger tube goes through the side of the cell right up to the stop-cock (C). The cell is a stoppered one and just below the stopper there is a side tube (S) which serves as an outlet for the exit gas.

The hydrogen obtained from pure zinc and sulphuric acid was purified by passing successively through acid and alkaline potassium permanganate solutions and silver sulphate solution and then through a  $\text{CaCl}_2$  tower to retain traces of the liquid mechanically carried over and partially to dry it. The gas-flow was regulated by means of a stop-cock at the rate of 1-2 bubbles per second. Rubber stoppers and joints were avoided as far as practicable. Velvet corks paraffined outside were used. 2 C c. of  $N/20\text{-NaOH}$  solution were introduced into the absorption cell.

The substance was weighed in a small platinum boat and placed at a distance of 40 mm. from the furnace end. Hydrogen was then allowed to pass through the tube for 5 minutes to remove the air within the tube. A tiny micro-burner was then placed at a distance of 40 mm. from the boat and moved gradually towards the boat. After 10-15 minutes the burner was placed just below the boat and kept for 5-10 minutes. Micro-burner was then replaced by a Bunsen burner which was then slowly moved towards the platinised asbestos which had been maintained at a red heat all along. Burner was then removed and hydrogen current continued for another 15 minutes to chase the gaseous products formed.

The absorption cell was then washed out from the top with cold water (boiled air-free) into a 50 c. c. stoppered Erlenmeyer flask containing  $N/100$ -iodine solution (10 c. c.) acidified with  $N/5\text{-HCl}$  (2 c. c.)

The excess of iodine was titrated with  $N/100$ -sodium thiosulphate solution from a micro-burette using starch as indicator. As  $N/100$ -sodium thiosulphate did not keep well it was obtained by diluting  $N/10$ -sodium thiosulphate solution prepared according to Watson by making the  $p_H$  between 9 and 9.5 by adding 3.8 g. of borax per litre of the thiosulphate solution, which was found on experience to be quite stable.

The following table gives a few results obtained with the apparatus described above.



Substance.	Wt. of the substance.	N/100-I <sub>2</sub> soln. consumed.	Sulphur	
			Found.	Calc.
Thiourea	2.154 mg.	5.65 c. c.	41.96%	42.10%
Thiocarbanilide	4.200	3.65	13.90	14.05
Thiobenzamide	3.500	5.05	23.08	23.35
1 : 4-Naphthylamine sulphonic acid with $\frac{1}{2}$ H <sub>2</sub> O	4.050	3.50	18.82•	18.81
Sulphanilic acid with 1 H <sub>2</sub> O	4.191	4.36	16.64 •	16.75
Amylmercaptan	9.600	18.34	30.56	30.77
Diethyl disulphide	1.825	6.02	52.79	52.46
Dipropyl disulphide	8.259	22.04	42.39	42.66

After 5 or 6 experiments the tube was burnt in a current of oxygen to regenerate the activity of the catalyst.

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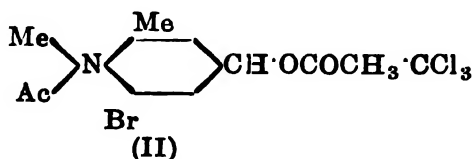
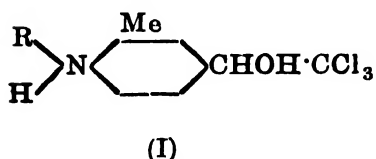
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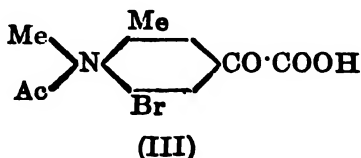
# Halogenation of the Condensation Products of Alkyl-*o*-toluidines with Chloral Hydrate and the Nitration of the Resulting Compounds.

By A. H. ADVANI.

With a view to study the nature of the reactions involved in the nitration of chloral derivatives of phenylalkylamines in which both the *ortho* positions to the amino group are occupied, bromination of the chloral derivatives of alkyl-*o*-toluidines (I, R=Me or Et) was carried out.



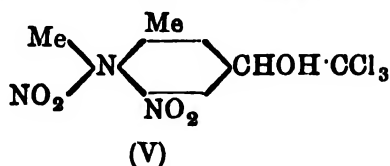
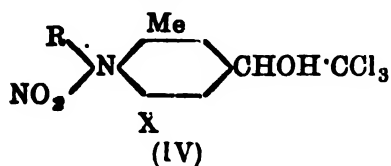
Bromine with (I) at ordinary or increased temperatures, with or without iodine as carrier, yielded only monobromo compounds. The position of the bromine atom was established from the fact that these monobromo compounds yielded diacetyl derivatives indicating that both chloral and the amino groups are not affected by the action of bromine. Moreover, the action of alkaline potassium permanganate on the diacetyl derivative of the monobromo compound (II) which should give a dibasic acid containing no bromine atoms if the latter entered the methyl group attached to the nucleus, yielded instead a ketonic acid (III), m.p. 201° containing bromine.



These reactions together with the work on the bromination of aromatic amines by Fries (*Annalen*, 1906, 346, 128) indicate that as in nitration, the bromine atom enters the nucleus in the *ortho* position to the amino group. With chlorine, products similar to the bromo compounds described above, were obtained. In this instance the basic chloral compounds gave impure substances, hence their hydrochlorides were taken for the reaction. The resulting

hydrochlorides were converted into the corresponding bases with ammonia. As with bromo compounds, the acetylation gave diacetyl derivatives.

Nitric acid with the halogenated products of the type (II) yielded bromo- and chloro-chloralphenylalkylnitroamines (IV, X=Br or Cl)



The constitution is confirmed by acetylation when the acetyl group enters the chloral side chain only.

When the nitration product (V) was heated with thionyl chloride, the hydroxyl group in the side chain was replaced by chlorine.

Hence from the study of the nitration of chloral derivatives of (i) alkyylanilines. (ii) alkyl-*o*-toluidines (*cf.* Advani and Wheeler, *Rec. trav. chim.*, 1933, **42**, 257), and (iii) the halogenation products of the latter at ordinary temperature without the use of a diluent, it was found that the compounds of the type (i) yielded chloral dinitrophenylalkylnitroamines, those of the type (ii) gave chloral mononitrophenylalkylnitroamines and the last only chlorophenylalkylnitroamines, the number of the entrant nitro groups depending upon the presence of replaceable hydrogen in the *ortho* position to the amino group.

#### EXPERIMENTAL.

**2-Methyl-4-( $\alpha$ -hydroxy- $\beta$ -trichloroethyl)-6-bromo-N-methylaniline.**—*p*-( $\alpha$ -Hydroxy- $\beta$ -trichloroethyl)-*o*-methyltoluidine (15 g.) and bromine (4.5 g.) were reacted in carbon tetrachloride solution. The resulting precipitate was filtered, washed with carbon tetrachloride and crystallised from dilute methyl alcohol in clusters of needles, m.p. 160°, yield 16.5 g. ( $\text{C}_{10}\text{H}_{11}\text{ONCl}_3\text{Br}$  requires Halogen, 58.7. Found: Halogen, 58.5 per cent).

The foregoing substance on acetylation gave clusters of prismatic needles from dilute ethanol of 2-methyl-4-( $\alpha$ -acetoxy- $\beta$ -trichloro-ethyl)-6-bromo-N-methylacetanilide, m. p. 180°. ( $\text{C}_{14}\text{H}_{15}\text{O}_3\text{NCl}_3\text{Br}$  requires Halogen, 48.2. Found: Halogen, 42.9 per cent).

**8-Methyl-4-(N-acetylmethylamino)-5-bromophenylketonic acid.**—The diacetyl derivative (10 g.) was treated at 100° with excess of a mixture of 5% potassium permanganate solution. The filtrate from the precipitated hydrated manganese dioxide, evaporated to half its

bulk, when acidified with strong hydrochloric acid, gave a product which crystallised from boiling water in feathery plates, m. p. 201°. (Found: Br, 25·2.  $C_{12}H_{12}O_4NBr$  requires Br, 25·5 per cent).

**2-Methyl-4-( $\alpha$ -hydroxy- $\beta$ -trichloroethyl)-6-bromo-N-ethylaniline.**—*p*-( $\alpha$ -Hydroxy- $\beta$ -trichloroethyl)-*o*-ethyltoluidine (10 g.) was treated with bromine (2·8 g.) and crystallised from dilute alcohol, m.p. 115°, yield 11·2 g. ( $C_{11}H_{13}ONCl_3Br$  requires Halogen, 51·6. Found: Halogen, 51·4 per cent).

The foregoing substance formed *acetyl* derivative as hexagonal plates from dilute methyl alcohol, m.p. 150-52°. ( $C_{13}H_{17}O_3NCl_3Br$  requires Halogen, 41·8. Found: Halogen, 42·1 per cent).

**2-Methyl-4-( $\alpha$ -hydroxy- $\beta$ -trichloroethyl)-6-chloro-N-methylaniline.**—The powdered hydrochloride of *p*-( $\alpha$ -hydroxy- $\beta$ -trichloroethyl)-*o*-methyltoluidine (16 g.) was suspended in dry benzene (50 c.c.) and dry chlorine passed through the mixture under stirring for  $\frac{1}{2}$  hour, yield 12 g. The base was obtained by treatment with ammonia and crystallised from dilute methyl alcohol, m.p. 132-33°. (Found: Cl, 47·1.  $C_{10}H_{11}ONCl_4$  requires Cl, 46·9 per cent).

The *acetyl* derivative crystallised from dilute methyl alcohol, m.p. 112°. (Found: Cl, 38·5.  $C_{14}H_{15}O_3NCl_4$  requires Cl, 38·3 per cent).

**2-Methyl-4-( $\alpha$ -hydroxy- $\beta$ -trichloroethyl)-6-chloro-N-ethylaniline.**—The powdered hydrochloride of *p*-( $\alpha$ -hydroxy- $\beta$ -trichloroethyl)-*o*-ethyltoluidine (20 g.) was treated with chlorine. The hydrochloride thus obtained was basified with ammonia and crystallised from dilute methyl alcohol as prismatic needles, m.p. 116-17°, yield 14 g. (Found: Cl, 44·6.  $C_{11}H_{13}ONCl_4$  requires Cl, 44·8 per cent.).

The *acetyl* derivative crystallised from dilute methyl alcohol, m.p. 155-56°. (Found: Cl, 35·2.  $C_{15}H_{17}O_3NCl_4$  requires Cl, 35·4 per cent).

**2-Methyl-4-( $\alpha$ -hydroxy- $\beta$ -trichloroethyl-6-bromophenyl)-N-methylnitroamine.**—2-Methyl-4-( $\alpha$ -hydroxy- $\beta$ -trichloroethyl)-6-bromo-N-methylaniline (5 g.) was treated with strong nitric acid (15 c.c.). The filtered precipitate was kept in *vacuo* over alkali for 48 hours and crystallised from dilute ethyl alcohol as prismatic needles, m.p. 280° (decomp.), yield 5 g. ( $C_{10}H_{10}O_3N_2Cl_3Br$  requires Halogen, 47·5. Found: Halogen, 47·2 per cent).

The *acetyl* derivative crystallised from dilute methyl alcohol, m.p. 107°. ( $C_{12}H_{12}O_4N_2Cl_3Br$  requires Halogen, 42·8. Found: Halogen, 42·6 per cent).

**2-Methyl-4- (  $\alpha$ -hydroxy- $\beta$ -trichloro ethyl ) - 6-bromophenyl-N-ethyl-nitroamine.**—2-Methyl-4-( $\alpha$ -hydroxy- $\beta$ -trichloroethyl)-6-bromo-*N*-ethyl-aniline (5 g.) when treated with strong nitric acid furnished after crystallisation from dilute ethyl alcohol thin needles, m.p. 198° (decomp.), yield 4 g. ( $C_{11}H_{12}O_3N_2Cl_3Br$  requires Halogen, 45.9. Found: Halogen 45.5 per cent.).

The *acetyl* derivative crystallised from dilute methyl alcohol, m.p. 127°. ( $C_{13}H_{14}O_4N_2Cl_3Br$  requires Halogen, 41.6. Found: Halogen, 41.7 per cent.).

**2-Methyl-4- (  $\alpha$ -hydroxy- $\beta$ -trichloroethyl )-6-chlorophenyl-N-methyl-nitroamine.**—2-Methyl-4-( $\alpha$ -hydroxy- $\beta$ -trichloroethyl)-6-chloro-*N*-methyl-aniline (5 g.) was treated with warm strong nitric acid (6 c.c.). The crystalline nitroamine which separated on cooling, crystallised from a mixture of acetone and dilute ethyl alcohol as clusters of small needles which change colour at 210° and decompose at 230°, yield 4.5 g. (Found: Cl, 40.5.  $C_{10}H_{10}O_3N_2Cl_4$  requires Cl, 40.8 per cent.).

The *acetyl* derivative crystallised from dilute ethyl alcohol as clusters of needles, m.p. 113°. (Found: Cl, 36.1.  $C_{12}H_{12}O_4N_2Cl_4$  requires Cl, 36.4 per cent.).

**2-Methyl-4- (  $\alpha$ -hydroxy- $\beta$ -trichloroethyl )-6-chloro-phenyl-N-ethyl-nitroamine.**—2-Methyl-4-( $\alpha$ -hydroxy- $\beta$ -trichloroethyl)-6-chloro-*N*-ethyl-aniline was treated with strong nitric acid and the mixture heated until nitrous fumes began to evolve when the solid nitroamine separated. It crystallised from a mixture of acetone, methyl alcohol and water in thin needles, m.p. 181°. (Found: Cl, 39.0.  $C_{11}H_{12}O_3N_2Cl_4$  requires Cl, 39.2 per cent.).

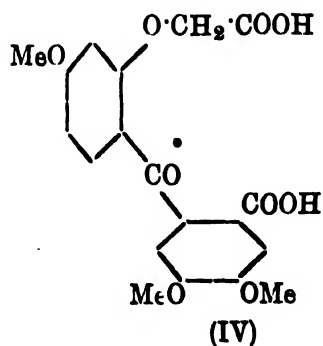
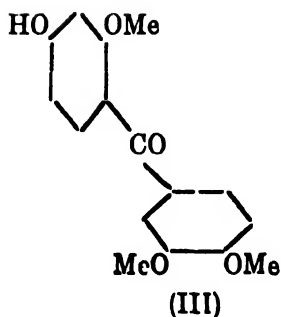
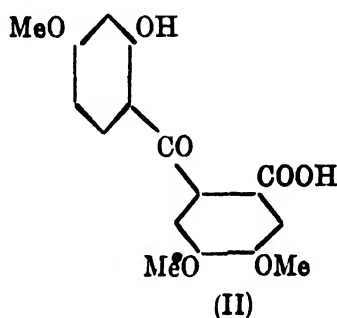
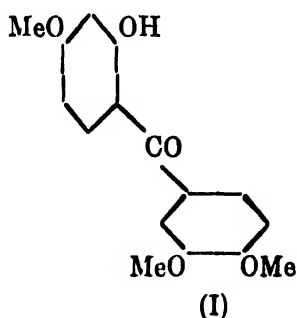
The *acetyl* derivative crystallised from dilute methyl alcohol in clusters of colourless needles, m.p. 182°. (Found: Cl, 35.0.  $C_{13}H_{14}O_4N_2Cl_4$  requires Cl, 35.1 per cent.).

**2-Methyl-4-( $\alpha$ -chloro- $\beta$ -trichloroethyl)-6-nitrophenyl-N-methylnitroamine.**—2-Methyl-4- (  $\alpha$ -hydroxy- $\beta$ -trichloroethyl ) - 6-nitrophenyl-*N*-methylamine (3 g.) was treated with thionyl chloride (15 c.c.) and the mixture refluxed on a water-bath at 50° for 3 hours. After removal of thionyl chloride, the thick liquid solidified in *vacuo* over alkali. It crystallised from absolute alcohol, m.p. 199°. (Found: Cl, 29.6.  $C_{10}H_9O_4N_3Cl_4$  requires Cl, 29.9 per cent.).

## A Synthesis of Brazilinic Acid.\*

BY J. NANENDRA NATH RAY, SANTOKH SINGH SILOOJA AND  
PREM RAJ WADHA.

The present structure of brazilin is dependent on the constitution of brazilinic acid which has been synthesised by Perkin and Robinson (*J. Chem. Soc.*, 1908, **93**, 515), by condensing *m*-hemipinic anhydride and ethyl methoxyphenoxyacetate in very poor yield. In the present paper it has been found that when ethyl methoxyphenoxypropionate is condensed with veratroyl chloride in presence of aluminium chloride there is extrusion of the ester grouping and the substance (I) along with (III) is produced. In view of this an alternative synthesis of brazilinic acid has been described here.



Perkin and Robinson (*loc. cit.*) found that hemipinic anhydride condensed unsatisfactorily with resorcinol dimethyl ether to give a

non-crystalline (chalky) precipitate of 2-hydroxy-4:4':5'-trimethoxybenzoylbenzoic acid (II). We have now prepared this substance from the ketone (I) by nitration, reduction and the subsequent replacement of  $\text{NH}_2$  by CN and finally hydrolysing the nitrile to the acid (II). The substance (I) was prepared by the Friedel and Crafts' reaction on *m*-methoxyphenol with veratroyl chloride, when the substance (III) was also formed in the reaction in almost equal amount. The respective structures were assigned after considering the ferric chloride reactions of the two ketones. The acid (II) was condensed with chloroacetic acid in alkaline solution when brazilin's acid (IV), identical with the acid from the natural product, was obtained.

#### EXPERIMENTAL.

**2-Hydroxy-4:4':5'-trimethoxybenzophenone.**—A solution of ethyl *m*-methoxyphenoxypropionate (4.2 g.), veratroyl chloride (4.1 g.) in nitrobenzene (10 c.c.) was cooled to  $0^\circ$  and was gradually treated with a solution of aluminium chloride (6 g.) in nitrobenzene (40 c.c.) with vigorous shaking. After standing for 12 hours, the mixture was decomposed and the solvent removed in steam. The sticky residue was treated in alcoholic solution with potassium hydroxide (2.6 g. in 30 c.c. alcohol) and the solution diluted with water and filtered. After acidification, the viscous mass obtained was crystallised twice from alcohol, m. p.  $141^\circ$ . (Found: C, 66.6; H, 5.6.  $\text{C}_{16}\text{H}_{16}\text{O}_5$  requires C, 66.7; H, 5.6 per cent). The substance gives a deep violet colour with ferric chloride solution. In one experiment a small amount of a substance (m. p.  $175^\circ$ ) was obtained. It is still under investigation but probably it is the substance (III) described below. The substance (m. p.  $141^\circ$ ) is identical with the product obtained as below.

Resorcinol monomethyl ether (5 g.) and veratroyl chloride (8 g.) dissolved in nitrobenzene (20 c.c.) were treated with a solution of aluminium chloride (8 g.) in the same solvent (50 c.c.) at  $0^\circ$ . After 3 hours, the temperature of the bath was raised to  $10\text{--}16^\circ$  and left for 18 hours with occasional shaking. The mixture after decomposition with ice was freed from the solvent by steam distillation and the non-volatile portion filtered hot. The insoluble portion crystallised from alcohol in pale yellow needles, m. p.  $141^\circ$ . The substance shows the strong violet ferric chloride reaction, dissolves in sodium hydroxide to an yellow solution and develops reddish yellow colour



with concentrated sulphuric acid. (Found: C, 66.5; H, 5.6.  $C_{16}H_{16}O_5$  requires C, 66.7; H, 5.5 per cent). The hot aqueous filtrate of the residue after steam distillation furnished a pale coloured crystalline deposit, m.p.  $175^\circ$  after recrystallisation from alcohol. (Found: C, 66.7; H, 5.3.  $C_{16}H_{16}O_5$  requires C, 66.7; H, 5.5 per cent). This substance (III) shows a much fainter ferric chloride reaction but otherwise possesses properties similar to the foregoing substance.

**2-Hydroxy-4 : 4' : 5'-trimethoxy-2-nitrobenzophenone.**—The substance (I) (1 g.) was dissolved in acetic acid (15 c.c.) by warming to  $60-70^\circ$  and then the solution cooled to  $50-53^\circ$ . 1.5 C.C. of a mixture of nitric acid ( $d$  1.42, 2 c.c.) and acetic acid (2.5 c.c.) and concentrated sulphuric acid (0.5 c.c.) was introduced with stirring, the temperature of the mixture being maintained at  $48-52^\circ$ . After 16 minutes, the nitro compound separated out and was collected after 2 hours. Crystallised from acetic acid it had m.p.  $211^\circ$  (Found: N, 4.5.  $C_{16}H_{15}O_7N$  requires N, 4.2 per cent). The structure follows from the fact that on oxidation it furnishes nitroveratric acid and energetic nitration gives dinitroveratrol.

**2-Hydroxy-4 : 4' : 5'-trimethoxy-2-aminobenzophenone hydrochloride** was prepared by reducing 1 g. of the foregoing nitro compound in alcohol (100 c.c.) with stannous chloride (6 g.), tin foil (1 g.) and concentrated hydrochloric acid (4–5 c.c.) on the steam bath for 15 minutes. After the removal of tin the solution was concentrated when the hydrochloride crystallised out. Recrystallised from alcoholic hydrochloric acid it had m.p.  $240^\circ$ . (Found: N, 4.2.  $C_{16}H_{18}O_5NCl$  requires N, 4.1 per cent).

**2-Hydroxy-4 : 4' : 5'-trimethoxy-2-cyanobenzophenone.**—A solution of the foregoing amine hydrochloride (1 g.) in hot water (80 c.c.) and hydrochloric acid ( $d$  1.16, 1 c.c.) was cooled to  $0^\circ$  and treated with 2.5 c.c. of 1% sodium nitrite solution. After treatment with potassium cuprocyanide and decomposition, the residue was extracted with alcohol whence the cyano compound (m.p.  $152-54^\circ$ ) was isolated. This was not analysed but directly employed in the subsequent operation.

**2-Hydroxy-4 : 4' : 5'-trimethoxybenzoylbenzoic acid (II)**—An alcoholic solution of the cyano compound isolated in the above experiment was heated with 10 c.c. of 80% sodium hydroxide solution on the steam-bath for 3-4 hours. After the removal of alcohol, the diluted solution was acidified and the precipitated acid was finally

crystallised from hot 80% acetic acid, m.p. 203°. (Found: C, 61.22; H, 4.68.  $C_{17}H_{16}O_7$  requires C, 61.44; H, 4.8 per cent).

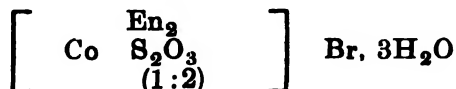
*Brazilinic acid* (IV).—(A) 2-Hydroxy-4:4':5'-trimethoxy-2-cyano-benzophenone (0.1364 g.) in water (5 c.c.) and 1% sodium hydroxide solution (1.75 c.c.) was treated with chloroacetic acid (0.047 g.) in water (5 c.c.), neutralised by sodium carbonate and refluxed for 7 hours, on the steam-bath. Finally concentrated hydrochloric acid (6 c.c.) was added and heated for further half an hour. After the removal of alcohol, the solids obtained were dissolved in baryta solution till the resulting mixture was slightly alkaline. The filtrate was treated with exact amount of sulphuric acid, boiled with a little acetic acid and filtered. From the filtrate, a substance, m.p. 208°-209° was isolated which revealed no difference when compared with brazilinic acid obtained from the oxidation of trimethyl-brazilin and had mixed m.p. 209°. It also developed the characteristic red colour with sulphuric acid.

(B) 2-Hydroxy-4:4':5'-trimethoxybenzoylbenzoic acid (II) (0.4 g.) in water (10 c.c.) was neutralised with sodium hydroxide solution (7.6 c.c. of 1%). To this a neutralised solution of chloroacetic acid (0.15 g.) in water (5 c.c.) was added and the mixture heated on the steam bath for 7 hours. After acidification the product was crystallised from hot dilute acetic acid, m.p. 208-209° and disclosed no difference when compared with the natural and synthetic brazilinic acid as described above.

## On the Thiosulphato-tetrammine-cobaltic Series. Part II. Constitution of Duff's Salt.

BY BHABESH CHANDRA RAY AND PULIN BIHARI SARKAR.

By the action of barium thiosulphate on a hot solution of carbonato-diethylenediamine-cobaltic bromide Duff (*J. Chem. Soc.*, 1922, 121, 450) obtained a thiosulphato-diethylenediamine-cobaltic bromide to which he gave the following constitution evidently on



the assumption that  $\text{S}_2\text{O}_3$  radical, divalent as it is, has substituted the  $\text{CO}_3$  group and has taken up two contiguous co-ordination positions. This view on the constitution of the above salt was not substantiated by any other proof.

The present authors have prepared the sulphate and nitrate of this series firstly, by double decomposition of Duff's salt with  $\text{Na}_2\text{SO}_4$  and  $\text{KNO}_3$  and secondly, by the action of ethylenediamine on the corresponding *trans*-thiosulphato-aquo-tetrammine-cobaltic salts (Sarkar and Das-Gupta, *J. Indian Chem. Soc.*, 1930, 7, 835). The products were identical and invariably contained water molecules in their composition.

Thus the sulphate was found to be  $\text{Co}_2\text{En}_4(\text{S}_2\text{O}_3)_2\text{SO}_4, 2\text{H}_2\text{O}$  and nitrate,  $\text{Co En}_2(\text{S}_2\text{O}_3)(\text{NO}_3), \text{H}_2\text{O}$ .

Two more salts of this series, namely the iodide and the thiocyanate have been prepared, having the molecular formulæ respectively,



The invariable presence of two molecules of water in the composition of the sulphate and one molecule in the composition of nitrate and iodide are rather significant.

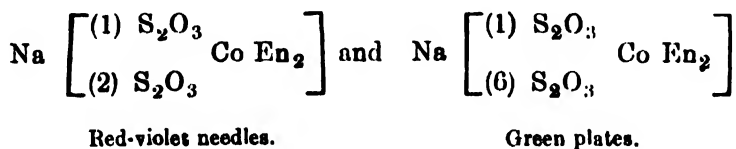
These compounds do not lose any water on drying over  $\text{H}_2\text{SO}_4$  in vacuum. It is difficult, *a priori*, to decide whether they are water of constitution or of crystallisation.

In order to decide this, we have taken recourse to analogy. Ray and his co-workers have prepared the compounds of thio-sulphato-pentammine-cobaltic ion (*J. Indian Chem. Soc.*, 1927, **4**, 64) as well as isomeric thiosulphato-pentacyano-cobaltic acids and their salts (*ibid.*, 1927, **4**, 325 ; *Z. anorg. Chem.*, 1931, **199**, 353), where  $S_2O_3$  radical has taken up one co-ordination position only.

Sarkar and Das-Gupta (*loc. cit.*) obtained, by the action of sodium thiosulphate on either *cis*-chloro-aquo or *trans*-dichloro-tetrammine cobaltic salts, *trans*-thiosulphato aquo-tetrammine series where also  $S_2O_3$  radical was proved to occupy one co-ordination position.

By the action of sodium thiosulphate on *cis*- and *trans*- dichloro-diethylenediamine-cobaltic chlorides, the authors have obtained two isomeric dithiosulphato-diethylenediamino-cobaltates of sodium, the former in red-violet needles and the latter in green rhombic plates.

The constitution of these salts are apparent from their synthesis They may be represented as :



In the above compounds thiosulphate radical has taken up, as is evident, only one co-ordination position. Molecular conductivity proves it to behave as a binary electrolyte.

The most interesting phenomenon observed in this case is the rapid transformation of the *cis* into *trans* modification, decidedly the stabler isomer. The transformation, in fact, was so rapid that the red-violet needles spontaneously changed into green plates even on exposure to air on microscope slides.

The *cis* variety was extremely hygroscopic and could only be kept in perfectly dry atmosphere.

The reciprocal transformation of green to red-violet salt can be effected in the following way :—The green solution is converted to pink red on adding NaOH from which by means of alcohol the red-violet salt can be obtained.

Ray and Maulik (*loc. cit.*) have simultaneously discovered these series by a totally different method (private communication).

We tried to prepare thiosulphato-complexes of the diammine series by the action of  $Na_2S_2O_3$  on dichloro-diaquo-diamino-

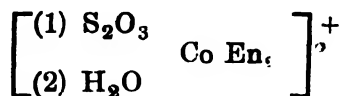
cobaltic chloride where a green compound was obtained in which the ratio of Co : S was found to be approximately 8.3. The ratio is slightly high. All attempts to isolate the pure salt failed, the salt spontaneously decomposing. The sodium salt separates out as an oil on adding alcohol from which it gradually crystallises.

The ratio of Co : S (1 : 8.3) indicates the probable composition  $\text{Na}_3 [\text{Co} (\text{S}_2\text{O}_3)_4 (\text{NH}_3)_2], \text{H}_2\text{O}$ . Evidently the thiosulphate radical has taken up one co-ordination position.

Moreover, the direct synthesis of Duff's salt from *trans*-thiosulphato-aquo-tetrammine-cobaltic salts and ethylenediamine speaks in favour of  $\text{S}_2\text{O}_3$  occupying one co-ordination position. From the colour of the salt it may be inferred that it is a *cis* compound. In the acido-tetrammine and diethylenediamine series the *trans* compounds are generally green whereas the *cis* compounds are violet to red-brown. The present compound is red-brown.

Whatever may be its constitution, be it *cis*-thiosulphato-aquo as suggested by us or *cis*-thiosulphato as given by Duff, it should be, according to theory, resolvable into optically active antipodes.

In our attempt to resolve Duff's salt with *d*-bromocamphor sulphonate as the active anion, we found the resulting sparingly soluble compound not to contain  $\text{S}_2\text{O}_3$  radical. In fact, the co-ordinated  $\text{S}_2\text{O}_3$  group is so very susceptible to hydrolysis that in course of double decomposition it comes out of the complex. This lends further support to our view that Duff's salt is a derivative of the monothiosulphato-aquo cation of the constitution



and not of  $\left[ \begin{array}{c} \text{S}_2\text{O}_3 \cdot \text{Co} \cdot \text{En}_2 \\ 1:2 \end{array} \right]^+$  as supposed by Duff.

Salts of the sulphato-tetrammine series have not yet been prepared. Job (*Bull. Soc. chim. Belg.*, 1923, 33, 4) has definitely proved that the so-called sulphate-tetrammine series are really sulphato-aquo-tetrammine compounds.

Duff (*J. Chem. Soc.*, 1922, 121, 52) claims to have prepared, sulphato-diethylenediamine-cobaltic bromide from  $(\text{CO}_3 \text{Co En}_2)\text{Br}$  with  $\text{H}_2\text{SO}_4$ .

The constitution proposed by him is  $\left[ \text{SO}_4 \text{ Co En}_2 \right] \text{Br, H}_2\text{O}$ .

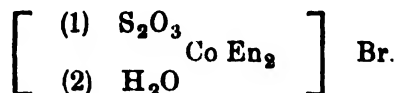
The invariable presence of one molecule of water is significant. In the light of Job's work certainly it is sulphate aquo compound.

Theoretically, there should be another isomer of Duff's salt of the constitution



Attempts to isolate it were unsuccessful, only *cis* compound was obtained. Similar observations were made by Werner during his study of the chloro-aquo and bromo-aquo-diethylenediamine series, only the *cis* salts were isolated.

Thus, in view of the facts cited above, Duff's salt should be represented by the formula



#### EXPERIMENTAL.

*Thiosulphato-diethylenediamine-cobaltic bromide* (Duff salt) was prepared according to the direction of Duff (*loc. cit.*, p. 450) by the action of barium thiosulphate on carbonate diethylene-diamine-cobaltic bromide, prepared by the method of Werner (*Annalen.*, 1912, 386, 100).

*Thiosulphato-aquo-diethylenediamine-cobaltic nitrate*.—Duff's salt (4.25 g.) was dissolved in water (15 c.c.) and filtered, solid  $\text{KNO}_3$  (2 g.) was added to the filtrate. On stirring and keeping in ice-bath dark-brown plates were obtained which were drained and washed with a little iced water. They were then recrystallised from water by evaporation in a vacuum over  $\text{H}_2\text{SO}_4$ . The salt was washed with absolute alcohol and dried in the air, yield 1.2 g. (Found: N, 18.92; S, 17.29; Co, 15.95.  $\text{Co} \cdot \text{S}_2\text{O}_3 \cdot \text{En}_2, \text{H}_2\text{O}$  requires N, 18.87; S, 17.25, Co, 15.90 per cent).

*Thiosulphato-aquo-diethylenediamine-cobaltic sulphate*.—Duff's salt (4.25 g.) was dissolved in 15 c.c. of water. To the clear solution of  $\text{Na}_2\text{SO}_4$  (2 g.) was added and stirred while keeping in ice-bath.

Dark brown plates were obtained. They were then drained and recrystallised as before, yield 1 g. [Found: S, 22.35; Co, 16.56 ( $\text{Co} \cdot \text{S}_2\text{O}_3 \cdot \text{En}_2 \cdot \text{H}_2\text{O}$ )<sub>2</sub> SO<sub>4</sub> requires S, 22.41; Co, 16.52 per cent].

*Thiosulphato-diethylenediamine cobaltic-iodide*.—Duff's salt (4.25 g.) was dissolved in the least quantity of water and finely powdered KI (1.7 g.) was added to the solution. Immediate precipitation of brown iodide took place. The mixture was stirred and kept in the ice-bath. After sometime the crystals were drained, washed first with a little ice water and then successively with 50% and 75% alcohol and finally with absolute alcohol. The salt was recrystallised from water in a vacuum, yield 2.1 g. [Found: N, 12.82; I, 29.02; S, 14.51; Co, 13.57. ( $\text{Co} \cdot \text{S}_2\text{O}_3 \cdot \text{En}_2 \cdot \text{H}_2\text{O}$ )I requires N, 12.82; I, 29.12; S, 14.68; Co, 13.63 per cent.].

*Thiosulphato-aquo-diethylenediamine-cobaltic thiocyanate*.—Duff's salt (4.25 g.) was dissolved in the minimum quantity of water and to it was added KSCN (1.5 g.). The mixture was kept in ice-bath. The crystals were drained, washed with dilute alcohol and finally with absolute alcohol. They were then crystallised as before, yield 1.4 g. [Found: N, 18.0; S, 25.0; Co, 15.16. ( $\text{Co} \cdot \text{S}_2\text{O}_3 \cdot \text{En}_2 \cdot \text{H}_2\text{O}$ ) SCN, H<sub>2</sub>O requires N, 18.18; S, 24.93; Co, 15.32 per cent].

*Synthesis of Duff's salt from trans-thiosulphato-aquo-tetrammine-cobaltic bromide*.—*trans*-Thiosulphato-aquo-tetrammine-cobaltic bromide (3.37 g.) prepared according to Sarkar and Das-gupta (*loc. cit.*) was treated with ethylenediamine solution (12 c.c. of 10%) and stirred. Strong smell of NH<sub>3</sub> was observed. After the elimination of NH<sub>3</sub> deep brown coloured plates were obtained. They were then drained, washed with a little iced water and finally with absolute alcohol. They were then recrystallised. [Found: N, 13.04; Br, 18.66; S, 15.19; Co, 13.80. ( $\text{Co} \cdot \text{S}_2\text{O}_3 \cdot \text{En}_2 \cdot \text{H}_2\text{O}$ ) Br, 2H<sub>2</sub>O requires N, 13.17; Br, 18.80; S, 15.09; Co, 13.88 per cent]. . .

*trans-Dithiosulphato-diethylenediamine-cobaltate of sodium*.—To an ice-cooled saturated solution of *trans*-dichloro-diethylenediamine cobaltic chloride (5 g.) a cold saturated solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (15 g.) was added. The mixture was kept in an ice-chest for 1 hour. The shining green plates were then drained, washed first with dilute alcohol and finally with absolute alcohol. They are rhombic plates, soluble in water. [Found: N, 15.52; S, 29.86; Co, 13.78; Na, 5.54. {Co (S<sub>2</sub>O<sub>3</sub>)<sub>2</sub> · En<sub>2</sub>} Na requires N, 15.54; S, 30.04; Co, 13.85; Na, 5.89 per cent].

*cis*-Dithiosulphato-diethylenediamine-cobaltiate of sodium.—To an ice-cold saturated solution of *cis*-dichloro-diethylenediamine-cobaltic chloride (5 g.) was added a solution of  $\text{Na}_2\text{S}_2\text{O}_3$  (15 g.) (made slightly alkaline with NaOH solution). The mixture was kept in an ice-bath. Red-violet needles separated, they were rapidly filtered, washed first with 50% and then with absolute alcohol. The salt was dried in a vacuum desiccator containing a little  $\text{Am}_2\text{CO}_3$ . The red-violet needles on exposure to air spontaneously change into green plates at the ordinary temperature. [Found: N, 15.80; S, 29.91; Co, 13.80; Na, 5.26.  $\text{Na Co}(\text{S}_2\text{O}_3)_2 \cdot \text{En}_2$  requires N, 15.54; S, 30.04; Co, 13.85; Na, 5.39 per cent].

*Attempt to prepare tetrathiosulphato-diamine salts of cobalt.*—To a well cooled solution of dichloro-diaquo-diamine-cobalt chloride, prepared according to Werner (*Ber.*, 1906 39, 1540) from Edmann's salt, was added a cold saturated solution of  $\text{Na}_2\text{S}_2\text{O}_3$  (calculated amount). The mixture was kept in an ice-chest. Immediately on mixing a green scum separated. This was rapidly separated by filtration and to the cold filtrate an excess of cooled alcohol was added. A green oil separated which was removed by means of a separating funnel. It was redissolved in water and fractionated by means of alcohol. Finally the oil was crystallised on stirring with large excess of absolute alcohol.

On examination through microscope the salt appeared uniform. The salt is very unstable and begins to decompose when dry. The still moist salt was analysed. The ratio of Co : S was found to be 1 : 8.3. Qualitative analysis showed the presence of sodium and ammonia.

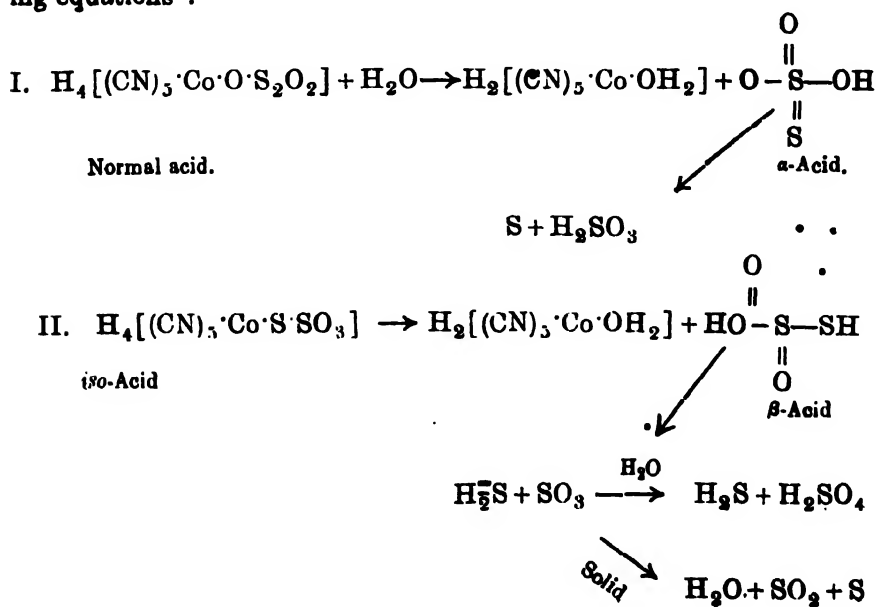
In any case, the ratio found corroborates the formation of tetrathiosulphato-diamine-cobaltiate ion and strongly supports our views that  $\text{S}_2\text{O}_3$  radical in complex cobaltiammines takes up only one co-ordination position.



# The Decomposition of Thiosulphato-pentacyano-cobaltic Acid and the Isomerism of Thiosulphuric Acid.

By PRIYADA RANJAN RÂY.

A report about the isolation of two isomeric modifications of the complex thiosulphato-pentacyano-cobaltic acid was published some two years ago (Rây, *Nature*, 1931, 127, 856 ; *J. Indian Chem. Soc.*, 1931, 8, 307) ; and a detailed account of the preparation, properties and constitution of the two modifications was given in a subsequent paper in the same year (Rây and Maulik, *Z. anorg. Chem.*, 1931, 199, 353). It was shown that the isomerism of the two acids is due to a difference in the constitution of the  $S_2O_3^{2-}$  radical contained in them, since, on hydrolysis, the two complex acids give rise to different varieties of thiosulphuric acid ; of which one decomposes as usual into S and  $H_2SO_3$ , while the other gives  $H_2S$  and  $SO_3$ . The two complex acids were termed normal and *iso*-acids respectively, and the corresponding thiosulphuric acids resulting from their hydrolysis as  $\alpha$ - and  $\beta$ -thiosulphuric acids. These facts, as already shown (Rây and Maulik. *loc. cit.*), can be represented by the following equations :



A quantitative study of this hydrolytic decomposition has also been made and this forms the subject matter of the present paper. The results obtained definitely support the above representation and confirm the constitution previously suggested for the two varieties of the acid.

The decomposition of the *iso*-acid was quantitatively studied by distilling the solid acid with dilute HCl. The liberated  $H_2S$  gas was absorbed in an ammoniacal cadmium salt solution. The precipitated CdS was dissolved in an excess of standard iodine solution, and the amount of sulphidic sulphur ( $H_2S$ ) was estimated as usual.

A yellowish brown slimy residue was left behind in the distilling flask. This was filtered and the amount of sulphuric acid ( $SO_3$ ) in the filtrate was estimated as  $BaSO_4$ .

The yellowish brown slimy residue, on treatment with NaOH solution, gave a bluish green residue of  $Co(OH)_2$  and a filtrate containing  $[Co(CN)_6]^{3-}$  ion. The slimy residue also contained free S as was proved by digestion with KCN solution and then testing for KSCN with  $FeCl_3$ . This proves that the slimy, yellowish brown residue is a cobaltous cobalticyanide. The Cobaltous compounds evidently resulted from the decomposition of the aquo-pentacyano-cobaltic acid, one of the products of hydrolysis of the complex *iso*-thiosulphato-pentacyano-cobaltic acid.

The filtrate from the slimy precipitate contained a simple cobaltous salt as  $CoCl_2$  or  $CoSO_4$ .

### RESULTS.

I. A sample of the *iso*-acid containing 18.3% Co gave on distillation with HCl:

$S''$  (sulphidic) = 4.14%; S (as  $SO_4''$ ) = 9.2%.

$\therefore Co : S'' : S(SO_4'') = 1 : 0.42 : 0.935$ .

II. Another sample containing 17.56% Co gave on distillation with HCl:

$S''$  (as  $H_2S$ ) = 5.38%; S (as  $SO_4''$ ) = 9.1%.

$\therefore Co : S'' : S(SO_4'') = 1 : 0.56 : 0.95$ .

III. A third sample containing 16.15% Co gave on distillation with acid:

$S''$  (as  $H_2S$ ) = 5.64%; S (as  $SO_4''$ ) = 8.1%.

$\therefore Co : S'' : S(SO_4'') = 1 : 0.642 : 0.928$ ,

The cobalt in the filtrate from the slimy precipitate was determined after precipitation of  $\text{H}_2\text{SO}_4$ . It contained 9.8 Co, i.e., about 60.7% of the total Co present in the *iso*-acid.

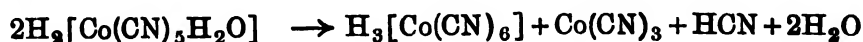
Similar results were obtained by distillation with water alone for a somewhat longer time.

The variation in the percentage of total Co in the different samples of the *iso*-acid was due to the difference in the water of hydration of the acid, (cf. Rây and Maulik, *loc. cit.*).

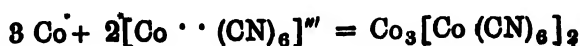
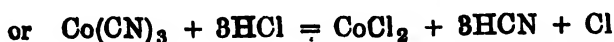
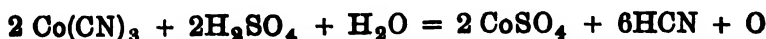
#### DISCUSSION.

Considering the equation II for the hydrolysis of the *iso*-acid, it follows that the proportion of Co : S'' : S( $\text{SO}_4$ ) should be 1 : 1 : 1. The estimated value for S as  $\text{SO}_4$  in all the samples examined is in fair agreement with this ratio, though the result is always lower (about 5.7%). This can be accounted for by the fact that the solid *iso*-acid undergoes a slight decomposition at the laboratory temperature (25-27°) with separation of S and  $\text{SO}_2$  (*vide* equation II).

The amount of sulphidic sulphur has not been found to exceed 64% of the theoretical value. This has to be accounted for. The sulphur present in the slimy precipitate evidently makes up this deficit, and the appearance of about 60% of the total Co of the *iso*-acid as Co'' in the filtrate from the slimy residue, as well as the formation of cobaltous cobalticyanide, are in perfect agreement with this fact. This becomes clear when we consider the decomposition of aquo-pentacyano-cobaltic acid, one of the primary products of hydrolysis of the *iso*-acid. The aquo-pentacyano-cobaltic acid, being not a very stable compound, undergoes decomposition in the boiling solution.



In the boiling solution, cobaltic cyanide decomposes into cobaltous sulphate and oxygen, or into cobaltous chloride and chlorine in the presence of HCl. The oxygen or the chlorine liberated acts upon  $\text{H}_2\text{S}$  which is thus oxidised to S and  $\text{H}_2\text{O}$ . The sulphuric acid and hydrogen sulphide are produced by the hydrolysis of  $\beta$ -thiosulphuric acid.



The presence of Co . . in the filtrate from the slimy precipitate and of S in the latter, as well as the defect of sulphur in the distillate, are thus clearly explained. The nature and composition of the slimy precipitate also agrees perfectly with this representation.

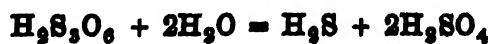
Bassett and Durrant (*J. Chem. Soc.*, 1927, 1416) have come to the conclusion that thiosulphuric acid decomposes according to the three reversible reactions :



Foerster (*Z. anorg. Chem.*, 1928, 177, 61) however, disagrees with the view that thiosulphuric acid leads to the formation of trithionic acid and  $\text{H}_2\text{S}$  by decomposition. Recently Prakke and Stiasny (*Rec. trav. chim.*, 1933, 52, 615) have shown that the decomposition of thiosulphuric acid proceeds in two directions depending on the  $p_{\text{H}}$  value of the solution: (1) formation of S and  $\text{H}_2\text{SO}_3$  and (2) formation of polythionates, mainly  $\text{S}_5\text{O}_6^{2-}$  (pentathionate).

They too, therefore, disagree with Bassett and Durrant's view (*loc. cit.*). In no case they have found that ordinary thiosulphuric acid give more than traces of  $\text{H}_2\text{S}$  by decomposition in solution. The liberation of  $\text{H}_2\text{S}$  from thiosulphuric acid under any circumstance is attributed by them to the isomeric form of thiosulphuric acid.

As a result of experimental observations regarding the decomposition of the above described complex acid, it can be concluded that thiosulphuric acid is capable of existence in two different isomeric forms,  $\alpha$ - and  $\beta$ -modifications. Of these the  $\alpha$ -form decomposes as usual into  $\text{H}_2\text{SO}_3$  and S, whereas the  $\beta$ -form gives rise to  $\text{H}_2\text{S}$  and  $\text{H}_2\text{SO}_4$  on decomposition. Because, in the experiments described above, almost quantitative formation of  $\text{H}_2\text{SO}_4$  cannot be accounted for according to Bassett and Durrant's second equation, unless it is assumed that the whole of the thiosulphuric acid decomposes in the sense of their second equation into  $\text{H}_2\text{S}$  and  $\text{H}_2\text{S}_3\text{O}_6$ , and the latter ( $\text{H}_2\text{S}_3\text{O}_6$ ) is then quantitatively hydrolysed into  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{S}$  (*cf. Bassett and Durrant, loc. cit.*) as follows :



That trithionic acid will thus completely hydrolyse in boiling acid solution without giving  $3\text{O}_2$  and S is rather unlikely, and direct evidence thereto is completely lacking.

Even assuming, after Bassett and Durrant, that thiosulphuric acid can decompose into  $\text{H}_2\text{S}$  and  $\text{H}_2\text{SO}_4$  through the intermediate formation of  $\text{H}_2\text{S}_3\text{O}_6$ , a complete quantitative decomposition of this type will naturally justify the conclusion that thiosulphuric acid can exist in a second isomeric modification differing from the usual form, which decomposes more or less quantitatively into  $\text{H}_2\text{SO}_3$  and S. The constitution of these two modifications has already been discussed in previous contributions (Rây, *loc. cit.*).

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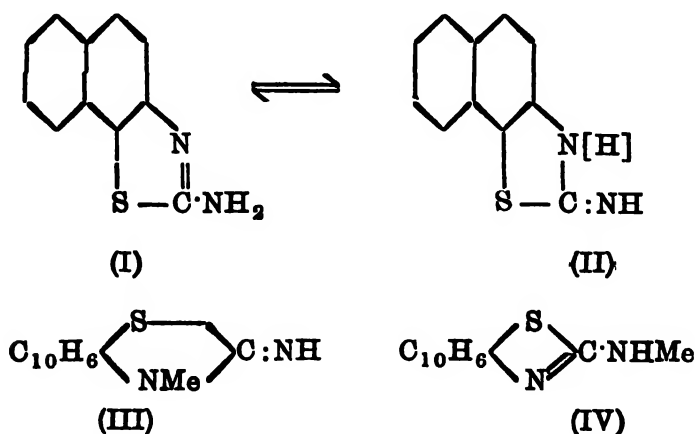
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**Studies in the Naphthathiazole Series. Part II.**  
**The Methylation of 1-Anilino- $\alpha$ -naphthathiazole**  
**and of 1-*p*-Bromoanilino- $\alpha$ -naphthathiazole.**  
**The Aromatic Character of the Hetero-**  
**cyclic Nucleus in  $\alpha$ -Naphthathiazoles.**

BY MAHMUDUR RAHAMN CHOWDHURY, RANCHHODJI DAJIBHAI  
 DESAI AND ROBERT FERGUS HUNTER.

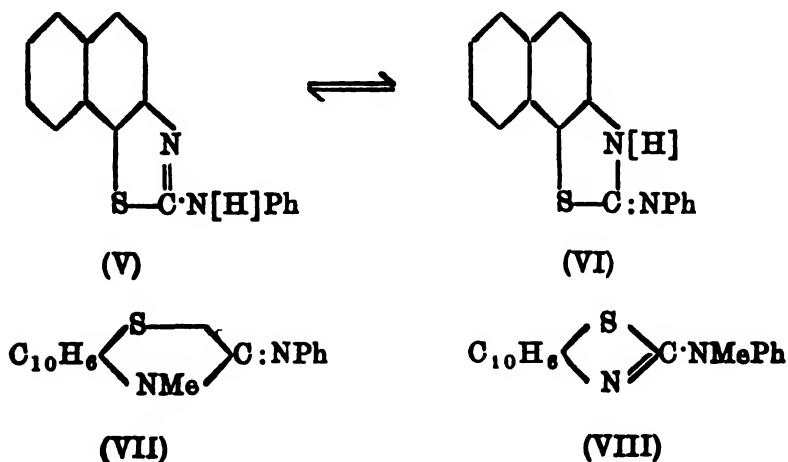
It has been shown that on methylation, 1-amino- $\alpha$ -naphthathiazole (I  $\leftrightarrow$  II) reacts exclusively in the amino phase yielding 1-imino-2-methyl-1:2-dihydro- $\alpha$ -naphthathiazole (III), unaccompanied by any detectable quantity of the isomeric methylamino- $\alpha$ -naphthathiazole (IV) (Hunter and Jones, *J. Chem. Soc.*, 1930, 941).



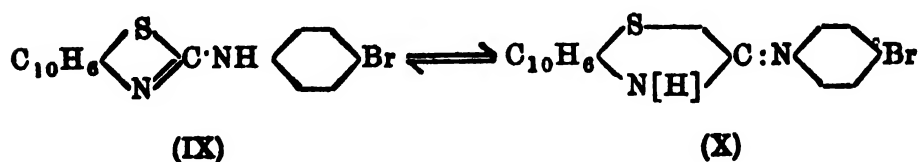
In the benzthiazole series, the reactivity of the semicyclic amidine system is also almost entirely in favour of the aminothiazole phase (Hunter, *J. Chem. Soc.*, 1926, 1385; Hunter and Styles, *ibid.*, 1928, 3019; Hunter and Pride, *ibid.*, 1929, 943). The introduction of a conjugated substituent such as the phenyl nucleus of the anilino grouping in 1-anilinobenzthiazole, however, enables the extra nuclear nitrogen atom of the triad system to compete with the heterocyclic nucleus for the double bond, with the production on methylation, of a mixture of isomeric methyl derivatives derived from both phases of the tautomeric system. This effect is

further enhanced by the presence of a *p*-bromosubstituent in the anilino grouping, since 1-*p*-bromoanilinobenzthiazole methylates apparently exclusively in the iminodihydrothiazole phase, yielding 4'-bromo-1-phenylmethylaminobenzthiazole (Hunter and Jones, *J. Chem. Soc.*, 1930, 2190).

It was, therefore, of interest to examine the effect of replacement of a hydrogen atom of the amino group in 1-amino- $\alpha$ -naphthathiazole by a phenyl radical on the reactivity of the semicyclic amidine towards alkylating agents, and the methylation of 1-anilino- $\alpha$ -naphthathiazole ( $V \leftrightarrow VI$ ) was investigated. On methylation by means of methyl iodide under conditions similar to those used in the case of 1-amino- $\alpha$ -naphthathiazole, however, this base reacted completely in the amino phase (V) yielding 1-phenylimino-2-methyl-1:2-dihydro- $\alpha$ -naphthathiazole (VII); no trace of the isomeric methylaminonaphthathiazole (VIII), which has been synthesised from 1-chloro- $\alpha$ -naphthathiazole and methylaniline, being capable of detection.



Since the attraction of the phenyl nucleus for the  $\alpha\beta$ -double bond in 1-anilino- $\alpha$ -naphthathiazole is evidently insufficient to overcome the effect of internal aromatic conjugation of the heterocyclic ring, the investigation was extended to the 1-*p*-bromoanilino derivative ( $IX \leftrightarrow X$ ).





1-*p*-Bromoanilino- $\alpha$ -naphthathiazole, however, behaved similarly to 1-anilino- $\alpha$ -naphthathiazole and methylated exclusively in the amino aromatic form (IX), yielding 1-*p*-bromophenylimino-2-methyl-1:2-dihydro- $\alpha$ -naphthathiazole unaccompanied by any detectable quantity of 1-*p*-bromophenylmethylamino- $\alpha$ -naphthathiazole.

It is, therefore, evident that neither the anilino substituent in 1-anilino- $\alpha$ -naphthathiazole nor the *p*-bromoanilino substituent in 1-*p*-bromoanilino- $\alpha$ -naphthathiazole, possess sufficient attraction for the double bond of the semicyclic triad system to overcome the effect of internal aromatic conjugation in the thiazole nucleus of the  $\alpha$ -naphthathiazole complex.

A similar condition obtains in the 2-aminothiazoles themselves, since both 2-anilino-4-methylthiazole (Young and Crookes, *J. Chem. Soc.*, 1906, 89, 59) and 2-*p*-toluidino-4-methylthiazole (Dyson, Hunter, Jones and Styles, *J. Indian Chem. Soc.*, 1931, 8, 147) react exclusively in the aminothiazole phase on treatment with methylating agents. It has furthermore been found that 2-*p*-bromoanilino-4-methylthiazole behaves similarly and yields 2-*p*-bromophenylimino-3:4-dimethyl-2:3-dihydrothiazole in exclusion to other products, on methylation under the usual conditions (Hunter and Parken, unpublished experiments).

The behaviour of the 1-amino- $\alpha$ -naphthathiazoles, therefore, resembles that of the simple aminothiazoles much more closely than that of the 1-aminobenzthiazoles, and the heterocyclic nucleus in  $\alpha$ -naphthathiazole is evidently more aromatic than in benzthiazole. The suggestion has been offered that a certain degree of aromatic character of the thiazole nucleus is lost when it is combined with a benzene ring as in benzthiazole due to the mutual effect of the aromatic nuclei, such as is witnessed in the naphthalene molecule (Dyson, Hunter, Jones and Styles, *loc. cit.*). If this is the case, it is clear that the disturbing effect of the benzene ring in benzthiazole is largely compensated by the presence of a second fused aromatic nucleus as in  $\alpha$ -naphthathiazole. This question cannot, however, be discussed until the behaviour of other combinations of the thiazole ring with the naphthalene system have been investigated.

#### EXPERIMENTAL.

1-Chloro- $\alpha$ -naphthathiazole was prepared by heating a mixture of  $\beta$ -naphthylthiocarbimide (4.6 g.) and phosphorus pentachloride

(5.2 g.) in sealed tube at 160—170° for 6 hours. The product was treated with water to decompose phosphorus halides and the mixture was extracted with chloroform and the chloroform was removed from the extract on a water-bath. The product obtained in this way had m.p. 79° and was pure enough for ordinary purposes (cf. Hunter and Jones, *J. Chem. Soc.*, 1930, 942)

1-Anilino- $\alpha$ -naphthathiazole was prepared by the condensation of 1-chloro- $\alpha$ -naphthathiazole and aniline, and separated from methyl alcohol-ethyl acetate in silky needles, m.p. 211–12°

*The methylation of 1-anilino- $\alpha$ -naphthathiazole, the isolation of 1-phenylimino-2-methyl-1:2-dihydro- $\alpha$ -naphthathiazole and the synthesis of 1-phenylmethylamino- $\alpha$ -naphthathiazole.*—(i) A mixture of 1-anilino- $\alpha$ -naphthathiazole (1 g.) and methyl iodide (2 c.c.) was heated in a sealed tube at 100° for 12 to 13 hours. The product was treated with warm 20% potassium hydroxide and the mixture was kept for 1 hour and thereafter extracted with chloroform. The base obtained by removal of the chloroform from a steam-bath was fractionally crystallised from alcohol, when 1-phenylimino-2-methyl-1:2-dihydro- $\alpha$ -naphthathiazole was obtained in glistening needles, m.p. 182°. (Found: S, 11.0.  $C_{18}H_{14}N_2S$  requires S, 11.0 per cent). This methylation product appeared to be quite homogeneous and all attempts to isolate any traces of the isomeric 1-phenylmethylamino isomer proved unsuccessful. The picrate was prepared by mixing benzene solutions of the base (0.3 g.) and picric acid (0.25 g.) and warming the mixture on a steam-bath for a few minutes; it separated from benzene in glistening golden yellow plates, m.p. 218°. (Found: S, 5.9.  $C_{18}H_{14}N_2S, C_6H_3O_7N_3$  requires S, 6.1 per cent).

(ii) A mixture of 1-chloro- $\alpha$ -naphthathiazole (0.6 g.) and methylaniline (0.3 g.) was heated in a boiling tube over a small naked flame until a violent reaction took place. The cold condensation product was treated with aqueous ammonia and the mixture was boiled, when a resinous product was obtained which became semi-solid on cooling in a freezing mixture. This was dissolved in methyl alcohol and the solution was concentrated in a vacuum at laboratory temperature when the base was obtained as an oil which was dissolved in dilute hydrochloric acid and reprecipitated by ammonia. Attempts to crystallise this product from methyl alcohol proved unsuccessful and it was, therefore, converted into the picrate by treatment with picric acid in benzene solution as in the

case of the phenyliminomethyl-dihydro isomer. The *picrate* of 1-phenylmethylamino- $\alpha$ -naphthathiazole separated from benzene in greenish yellow plates, m.p.  $184^{\circ}$ . (Found: S, 6.2.  $C_{18}H_{14}N_2S$ ,  $C_6H_5O_7N_3$  requires S, 6.1 per cent). A mixture of this with the *picrate* of 1-phenylimino-2-methyl-1:2-dihydro- $\alpha$ -naphthathiazole melted at  $170-74^{\circ}$ . A search of the mother liquors for traces of this *picrate* in an experiment, in which the whole of the methylation product of 1-anilino-naphthathiazole was dissolved in benzene and converted into *picrate*, proved fruitless.

*Methylation of 1-p-bromoanilino- $\alpha$ -naphthathiazole, the isolation of 1-p-bromophenylimino-2-methyl-1:2-dihydro- $\alpha$ -naphthathiazole and the synthesis of 1-p-bromophenylmethylamino- $\alpha$ -naphthathiazole.*  
—1-p-Bromoanilino- $\alpha$ -naphthathiazole was prepared by condensation of equimolecular proportions of 1-chloro- $\alpha$ -naphthathiazole and *p*-bromoaniline, and had m.p.  $256^{\circ}$  after recrystallisation from alcohol—ethyl acetate (Hunter and Jones recorded m.p.  $250^{\circ}$ ).

(i) A mixture of 1-p-bromoanilino- $\alpha$ -naphthathiazole (0.6 g.) and methyl iodide (1 c.c.) was heated in a sealed tube at  $100^{\circ}$  for 16 hours, and the product was basified with boiling 20% sodium hydroxide and extracted with chloroform. After removal of the chloroform and recrystallisation from alcohol, 1-p-bromophenylimino-2-methyl-1:2-dihydro- $\alpha$ -naphthathiazole was obtained in glistening plates, m.p.  $182^{\circ}$ . (Found: Br, 22.4.  $C_{17}H_{13}N_2BrS$  requires Br, 22.2 per cent). A careful search of the mother liquors failed to reveal any trace of the isomeric 1-p-bromophenylmethylamino isomer.

(ii) *p*-Bromomethylaniline was prepared with some difficulty by the following method. Acetic anhydride (20 c.c.) was added to methylaniline (20 g.) and the mixture was thereafter heated on a sand-bath under reflux for 25 hours. On concentration, methylacetanilide solidified and had m.p.  $102^{\circ}$  after being dried on porous earthenware. A solution of this acetyl derivative (27.8 g.) in glacial acetic acid (100 c.c.) was treated with bromine (5 c.c. in 5 c.c. of the same solvent) in sunlight, when shining plates separated in the mixture during the course of 2-3 hours. The mixture was kept at laboratory temperature for a further 5 hours, diluted with water (4 vols.) and kept overnight when an oil separated which was extracted with ether. The viscous product obtained after removal of the ether was dissolved in concentrated hydrochloric acid and the mixture was heated on a sand-bath

under reflux for 5 hours, cooled and basified when *p*-bromomethylaniline separated as an oil which was extracted with ether. A mixture of 1-chloro- $\alpha$ -naphthathiazole (0.5 g.) and *p*-bromomethylaniline (0.6 g.) was gently heated over a small flame until a violent reaction took place and the cooled product was basified with ammonia. The *p*-bromophenylmethylamino base was extracted with ether and the product obtained by removal of the ether was recrystallised with some difficulty from alcohol, when it formed small crystals, m.p 245°. (Found: Br, 22.3.  $C_{17}H_{13}N_2BrS$  requires Br, 22.4 per cent).

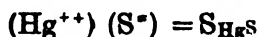
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## Conditions for the Potentiometric Titration of Copper with Sodium Sulphide and Use of Platinum Electrode.

BY JANG BAHADUR JHA.

Owing to the extremely low solubility of many metallic sulphides, their potentiometric titration with sodium sulphide attracted an early attention. During these titrations, mercury was chosen as an indicator electrode because reversible electrodes for a large number of metals are difficult to prepare. The working of the mercury electrode is simple. Mercury ions which are sent into the solution combine with the sulphide ions forming sparingly soluble mercury sulphide. The concentration of  $\text{Hg}^{++}$  and consequently the electrode potential is solely determined by the relation



Thus the mercury electrode acts as an indicator for the sulphide ions.

Using the above electrode Pinkhof (*Dissert. Amsterdam*, 1919) and other workers titrated many metals with sodium sulphide but the results were in general unsatisfactory. Even the compensation electrode method devised by Pinkhof failed to give satisfactory results. Thus when copper was titrated in presence of dilute sulphuric acid with silver in 0.5N-NaCl as compensation electrode the error amounted to 10%: subsequently when the titration was carried on in presence of a bicarbonate and tartaric acid the error reduced to 3%. The failure to obtain more accurate results has been attributed to the peculiar nature of the sulphides and to the great adsorption that takes place during their precipitation (Kolthof and Furman, "Potentiometric Titrations," 1926, p. 198).

It was accidentally found that a plain platinum wire could be used as an indicator electrode in place of the mercury electrode described above, in titrations with sodium sulphide. Consequently a platinum wire of 8 mm. diameter was used throughout the titrations given below.

But the chief reason for the large percentage of error and inconsistent results was found to be the presence of free mineral acids which were added to the metallic salt solutions. Even the presence of acetic acid has a considerable effect on the results. In an experiment varying amounts of a 0.38N-acetic acid were added into several beakers each containing 25 c.c. of copper sulphate solution (0.01527 g. of copper per 25 c.c.), and then titrated with standardised sodium sulphide solution. It was found that the amount of the reagent required to reach the end point increased with the amount of the acetic acid. The results are given in Table I.

TABLE I.

Acetic acid (c.c.)	... 0	1	2	3	4	5
Na <sub>2</sub> S required (c.c.)	... 27.67	27.94	28.18	28.29	28.41	28.56
Deviation from the calc. vol. of the sulphide (%)	... -0.8	-0.1	+0.7	+1.1	+1.6	+2.0

The strength of the sodium sulphide solution was determined by the Treadwell and Myr's method (*Z. anorg. Chem.*, 1915, 92, 127).

The results have been plotted in Fig. 1 from which it is seen that the error increases almost linearly with the amount of the free acid

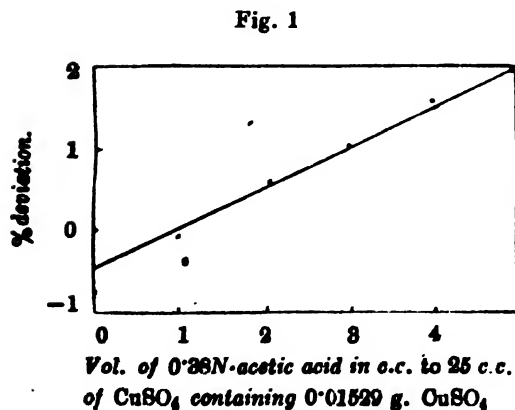
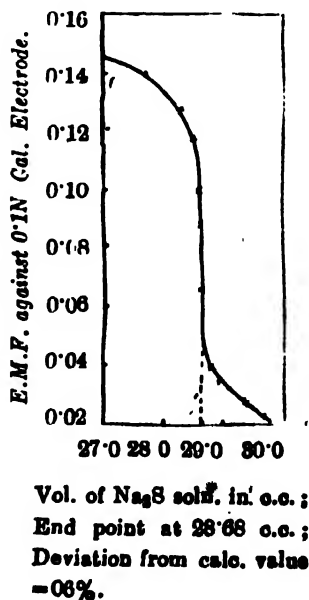


Fig. 2.



and it is least when 1 c.c. of the acid was present in 25 c.c. of the copper sulphate solution. The presence of sodium acetate is favourable for the estimation.

In practice it has been found that the proportion of the acetic acid to that of copper can be varied within certain limits. For solutions containing up to 12 g. of copper sulphate per litre, 1 c.c. of about 0.4*N*-acetic acid per 25 c.c. of the solution gives results with least error. For solutions of higher concentrations, greater amounts of acetic acid are necessary.

Another point which deserves attention is that the sodium sulphide which is used as the precipitating reagent in these titrations is rarely available in a pure state; it more often contains varying amounts of sulphite which reacts on the hydrogen sulphide and thus introduces a positive error. Even the best qualities available are not free from it. Freshly prepared sodium sulphide according to Böttger's directions has been found satisfactory (Böttger, *Annalen*, 1884, 223, 385) and the solutions can be prepared by weighing the requisite quantity and dissolving it in the necessary volume of freshly prepared distilled water and then standardised. In order to preserve the strength of sodium sulphide solution it was found necessary to keep it under hydrogen. An arrangement similar to that used for titrations with titanous salts was used (Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis", 1925, p. 63). The sodium sulphide solutions show a certain change in their strength during first 48 hours even under hydrogen after which period they have been found to retain their strength at least for 3 weeks. The standardisation should be done after this period.

Standardisation of sodium sulphide solution was done by direct titration with a copper sulphate solution containing a known amount of copper, although Treadwell and Myr's method may be used. A weighed piece of analytical copper was dissolved in dilute sulphuric acid containing a few c.c. of nitric acid. After warming to drive off nitric acid and its fumes the contents were diluted and the excess of the acid neutralised with caustic soda solution till a permanent green precipitate was obtained. Proper amount of the acetic acid was then added and the solution made up to a known volume. It was then titrated with the sodium sulphide solution to be standardised.

The method has been tested by making a large number of titrations with copper sulphate solutions of different strengths. The

potential attends steadiness soon after adding the reagent and shaking. The abrupt change at the end point is well marked. The copper sulphate solutions for titrations were prepared either from copper sulphate A.R. (B.D.H.) or from copper foil. The results of gravimetric and electroanalytical methods (Sand, *J. Chem. Soc.*, 1907, 41, 63) were taken to represent the actual amount of copper in the solution. Some of the results of titrations are given in Table II.

TABLE II.

Found Cu in 25 c.c. of the sol.	Actual Cu in 25 c.c.	Error.	Found Cu in 25 c.c. of the sol.	Actual Cu in 25 c.c.	Error.
0.3016 g.	0.3018 g.	-0.06%	0.09435 g.	0.09415 g.	+0.06 %
0.2626	0.2623	+0.1	0.01528	0.01527	+0.2
0.1990	0.1985	+0.2	0.007125	0.007095	+0.4
0.1518	0.1516	+0.1	0.005592	0.005580	+0.2
0.1154	0.1152	+0.2	0.005385	0.005345	+0.7

The above figures show that for solutions up to  $M/100$  dilution (approximately) the maximum error is 0.2 %, it however increases on further dilution. The error is most likely due to the presence of oxygen in distilled water. It is also significant to note that the error is in every case positive except the first one. If the solutions be made in distilled water free from dissolved gases, and the titrations carried on in an atmosphere of nitrogen, the error is likely to be eliminated or further reduced.

The characteristic titration curve is shown in Fig 2. It is to be observed that the potentials after the inflexion become unsteady and further prolongation of the curve was found to be impossible. But this is no hindrance in locating the end point.

The use of the platinum electrode in such titrations lacks theoretical foundation. The only other instance of this kind where Pt-electrode has been used, is for titration of silver nitrate with alkali halides (*cf.* Müller, *Z. Elektrochem.*, 1924, 30, 419). As an explanation, it has been assumed that the wire becomes coated with the metal during the titration (Kolthof and Furman, *ibid.*, p. 102). It is expected that further work will show that in titrations with sodium sulphide the potential of the platinum wire is due jointly to the concentrations of  $H^+$  and  $S^{2-}$  ions. The observed unsteadiness will then be ascribed to the escaping of the hydrogen sulphide after all the metal has been precipitated.



## SUMMARY.

1. The effect of free acetic acid in the titrations of copper sulphate with sodium sulphide has been studied.

2. It is shown that by regulating the amount of free acetic acid, copper can be titrated potentiometrically with a platinum electrode.

3. The view is suggested that the potential at the platinum electrode in the above case depends on the activities of hydrogen and sulphur ions.

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*Received August 7, 1933.*



# Reaction between Potassium Oxalate and Iodine and the Relation between Intensity and Velocity.

By W. V. BHAGWAT.

Dhar (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, 18, 1084) was the first to investigate kinetics of the reaction between potassium oxalate and iodine in light as well as in dark and he observed that the velocity of the reaction is greatly accelerated by light and is greater in sunlight than in diffused light. Later on Berthoud and Bellenot (*Helv. Chim. Acta*, 1924, 7, 307) investigated the same reaction and found it to be proportional to the square root of the incident radiation and this conclusion is supported by Briers, Chapman and Walters (*J. Chem. Soc.*, 1928, 562). Mukherji and Dhar (*J. Phys. Chem.*, 1928, 32, 1308) observed that the reactions between potassium oxalate and iodine, and ammonium oxalate and iodine are proportional to the square root of the incident radiation in presence of white light obtained from 1000 watt gas filled tungsten filament lamp and also of radiation of wave-length 4725Å. Recently Bhattacharya and Dhar (*J. Indian Chem. Soc.*, 1929, 6, 475) have investigated the same reaction in radiations of wave-lengths 5650Å and 7304Å using different intensities. They have used potassium iodide and free iodine.

The author has also studied this reaction in dark and in light of various wave-lengths and established the relation between intensity and velocity for this photochemical reaction in various regions. The results are tabulated below.

## Dark reaction.

$I_2 = 0.00256M$ .  $KI = 0.2306M$ .  $K_2C_2O_4 = 0.7595M$ . Temp. = 28°.

t.	Thiosulphate required.	$K_1 = 1/t \times \log a/a-x$ .
0 min.	9.1 c.c.	—
1125	7.7	0.0000644
3900	5.1	0.0000644

Mean  $K_1 = 0.0000644$

$K_1$  calculated as  $k_1 = 0.000440$ .

*Temperature coefficient of the dark reaction.*

Temp.	$K_1$ .	Temp. coeff. $K_1(38^\circ)/K_1(28^\circ)$ .
28°	0·0000644	—
38°	0·000442	6·86

Also  $K_2 = K_1 E / R \left( \frac{-T_2 - T_1}{T_1 T_2} \right)$ . Therefore  $E = 86240$  Calories.  $K_1$  at 38° calculated as  $k_{\frac{1}{2}} = 0·00302$ .

*Relation between intensity and velocity.*

(1) *Source* = total light from 1000 watt lamp. Temp. = 28°.

Diameter of the aperture = 2cm.

$t$ .	Thiosulphate required.	$k_{\frac{1}{2}} = 2/t (\sqrt{a} - \sqrt{a-x})$ .
0 min.	10·2 c.c.	
10	8·4	0·058
21	6·6	0·059
33	4·9	0·059
		<hr/> $K_{\frac{1}{2}} \text{ mean} = 0·0586$
diameter of the aperture.	$k_{\frac{1}{2}} = 2/t (\sqrt{a} - \sqrt{a-x})$ .	Purely photochemical $k_{\frac{1}{2}}$ .
2 cm.	0·059	0·05836
1"	0·040	0·03956
0·5"	0·0285	0·0280
Ratio of intensities.	Ratio of velocities.	Ratio of $\sqrt{\text{Intensities}}$ .
$(2/1)^2 = 4$	$\frac{0·05856}{0·03956} = 1·48$	2
$(1/0·5)^2 = 4$	$\frac{0·03956}{0·0280} = 1·41$	2
$(2/0·5)^2 = 16$	$\frac{0·05856}{0·0280} = 2·09$	4

# REACTION BETWEEN POTASSIUM OXALATE AND IODINE 651

Temp. = 38°.

Diameter of the aperture.	$k_{\frac{1}{2}} = 2/t (\sqrt{a} - \sqrt{a-x})$ .	Purely photochemical $k_{\frac{1}{2}}$ .
2 cm.	0.202	0.199
1"	0.1850	0.182
0.5"	0.0862	0.0832.
Ratio of intensities.	Ratio of velocities.	Ratio of $\sqrt{\text{Intensities}}$ .
$(2/1)^2 = 4$	$\frac{0.199}{0.132} = 1.50$	2
$(1/0.5)^2 = 4$	$\frac{0.132}{0.0832} = 1.58$	2
$(2/0.5)^2 = 16$	$\frac{0.199}{0.0832} = 2.4$	4

*Temperature coefficient of the reaction in total light.*

Diameter of the aperture.	$k_{\frac{1}{2}}$ at 28°.	$k_{\frac{1}{2}}$ at 38°.	Temp. coeff. $K_{\frac{1}{2}} (38^\circ)/K_{\frac{1}{2}} (28^\circ)$ .
2 cm.	0.0585	0.109	3.4
1 cm.	0.0395	0.132	3.4

(2) Source = 5750 Å

Light filter—nitrosodimethylaniline +  $\text{Ni}(\text{NO}_3)_2$  2.08M each in 1 cm. cell. Range of transmission = 5200—6800 Å. Mean  $\lambda = 5750\text{Å}$ . Maximum %  $T = 0.10$  (Bhagwat and Dhar, *J. Phys. Chem.*, 1931, 35, 2401). Diameter of the aperture = 2 cm. Temp. = 38°.

t.	Thiosulphate required.	$k_{\frac{1}{2}} = 2/t (\sqrt{a} - \sqrt{a-x})$ .
0 min.	10.6 c.c.	—
10	9.6	0.0305
20	8.8	0.0305
40	7.0	0.0305
		Mean $k_{\frac{1}{2}} = 0.0305$

Diameter of the aperture.	$k_{\frac{1}{2}} = 2/t (\sqrt{a} - \sqrt{a-x})$ .	Purely photochemical $k_{\frac{1}{2}}$ .
2 cm.	0.0305	0.0275
1	0.0160	0.0130
Ratio of intensities.	Ratio of velocities.	Ratio of $\sqrt{\text{intensities}}$ .
$(2/1)^2 = 4$	$\frac{0.0275}{0.0130} = 2.11$	2

(3) Source = 6700 Å.

Light filter—methyl violet 0.100 g. in 100 c. c. +  $K_2CrO_4$  5.6882N. Normal solution being expressed as  $\frac{K_2CrO_4}{2}$ ; each in 1 cm. cell. Range of transmission = 6280–7200 Å. Maximum %  $T = 56$  (Bhagwat and Dhar, *J. Phys. Chem.*, 1931, 35, 2391). Temp. = 38°

Diameter of the aperture.	$k_{\frac{1}{2}} = 2/t (\sqrt{a} - \sqrt{a-x})$ .	Purely photochemical $k_{\frac{1}{2}}$ .
2 cm.	0.0433	0.0403
1	0.0232	0.0202
Ratio of intensities.	Ratio of velocities.	Ratio of $\sqrt{\text{intensities}}$ .
$(2/1)^2 = 4$	$\frac{0.0403}{0.0202} = 2.0$	$\sqrt{4} = 2$

(4) Source = 8500 Å infra red.

Light filter— $K_2Cr_2O_7$  0.513 M in 1 cm. cell + 4 cobalt glasses (Bhagwat and Dhar, *J. Indian Chem. Soc.*, 1930, 7, 911). Temp. = 38°.

Diameter of the aperture.	$k_{\frac{1}{2}} = 2/t (\sqrt{a} - \sqrt{a-x})$ .	Purely photochemical $k_{\frac{1}{2}}$ .
2 cm.	0.0186	0.0156
1	0.00987	0.00687
Ratio of intensities.	Ratio of velocities.	Ratio of $\sqrt{\text{intensities}}$ .
$(2/1)^2 = 4$	$\frac{0.0156}{0.00687} = 2.27$	2

The results of the relation between intensity and velocity are summarised in the following table.

Source.	Range of transmission.	Ratio of intensities.	Ratio of $\sqrt{\text{intensities}}$	Ratio of velocities.
1000 watt lamp	...	$(2/1)^2 = 4$	2	1.48
„	...	$(1/0.5)^2 = 4$	2	1.41
„	...	$(2/0.5)^2 = 16$	4	2.09
5750 Å	5200-6300 Å	$(2/1)^2 = 4$	2	2.0
6700 Å	6280-7200 Å	$(2/1)^2 = 4$	2	2.11
8500 Å	...	$(2/1)^2 = 4$	2	2.27

The table clearly shows that the relation between intensity and velocity is not constant but as the velocity of the reaction decreases, the relation steadily rises from less-than under-root to under-root. Usually photochemical acceleration falls with increasing wave-length but in case of nitrosodimethylaniline and  $K_2CrO_4$  as light filters, because the intensity of the transmitted light is very low, maximum being only 0.1 %, the velocity constant is less than that of 6280-7200 Å and consequently the ratio of intensity and velocity is higher.

Berthoud and Bellenot (*loc. cit.*) observed the temperature coefficient for  $10^\circ$  between  $25^\circ$  and  $40^\circ$  to be 3.22 and 3.15 in red and blue light respectively. Berthoud (*Trans. Faraday Soc.*, 1931, 27, 484) has repeated his experiments and observed that his results do not agree with his previous work and also with that of Dhar (*loc. cit.*).

My results of the dark temperature coefficient and the value of  $E$  calculated shows that Dhar's results are quite reproducible. Very recently Young and Style have investigated the same reaction (*Trans. Faraday Soc.*, 1931, 27, 493) and claim to have confirmed the results of Berthoud and Bellenot (*loc. cit.*) and have observed that the value is at minimum in the neighbourhood of 579  $\mu\mu$ . In view of Berthoud's observations these values seem to be doubtful. Moreover, the extinction for this reaction increases as the wave-length falls. It is usually observed that as the frequency of the incident radiation increases, the temperature coefficient falls. Hence Young and Styles' observations must be taken with caution,

According to Bhattacharya and Dhar (*J. Indian Chem. Soc.*, 1929, **4**, 197, 493), the relation between intensity and velocity can show a relationship which is less than or greater than the direct, depending on the amount of acceleration. The present author (*Z. anorg. Chem.*, 1981, **199**, 412 ; *U. P. Acad. Sci.*, 1981, **1**, 54) has deduced a theoretical expression connecting velocity with intensity and has shown that this relationship can never exceed the direct. This view is borne out by the above results.

My best thanks are due to Prof. N. R. Dhar for his kind interest in this paper.

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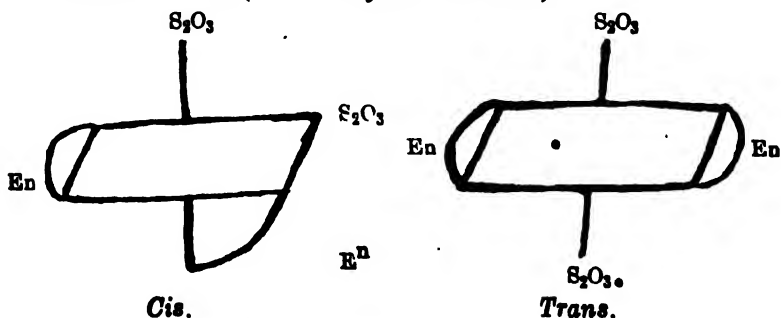


## Dithiosulphato-diethylenediamine-cobaltiates.

BY PRIYADA RANJAN RÂY AND SAILENDRA NATH MAULIK.

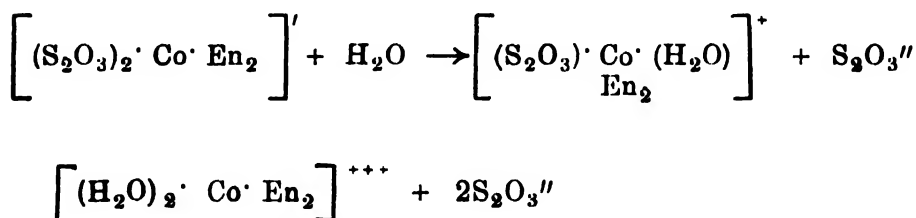
Preparation of thiosulphato-cobalt complexes, such as thiosulphato-pentammine-cobaltic salts and thiosulphato-pentacyano-cobaltiates, has already been reported in some previous papers (Rây, *J. Indian Chem. Soc.*, 1927, **4**, 64, 325; Rây and Maulik, *Z. anorg. Chem.*, 1931, **199**, 853). In these, the complex ionic group contained only one thiosulphate radical. It was expected that complexes containing two thiosulphate radicals would result if ammonia could be replaced by a twofold co-ordinating unit or a "chelate" molecule like ethylenediamine in the general method of preparation of thiosulphato-cobalt-ammines (Rây, *loc. cit.*). This has actually been realised and forms the subject matter of the present paper. By a method similar to that employed for the preparation of thiosulphato-pentammine-cobaltic chloride and using ethylenediamine in place of ammonia, a series of dithiosulphato-diethylenediamine-cobaltiates of the general formula  $M [Co \cdot (S_2O_3)_2 \{C_2H_4(NH_2)_2\}_2]$  have been prepared: where  $M = Na, K, \text{ or } Tl$ . In these, the bivalent thiosulphate radical fills up only one co-ordination position as in the previously described thiosulphato-complexes.

A compound of the above composition is likely to exist in two different isomeric forms (*cis* and *trans*), due to a difference in the space distribution of the constituent radicals around the central Co atom, as shown below (En = Ethylene diamine).



Both these isomeric forms have been isolated. The green *trans* salts are more stable under ordinary circumstances, but are transformed into the red *cis* modification in alkaline solutions. The *cis* modification again, as is well known, is capable of resolution into two

optically active enantiomerides. Attempts to resolve the *cis* sodium salt with active strychnine nitrate led to the decomposition of the thiosulphato-complex as the solution of strychnine nitrate reacts acid due to hydrolysis, and the thiosulphato-complexes are very sensitive to acids. The employment of a neutral active body like *d*-triethylenediamine-cobaltic bromide in place of strychnine nitrate did not give any better result. In this case the sparingly soluble triethylenediamine-cobaltic thiosulphate separated out from the solution on evaporation. This indicates that the complex dithiosulphato-diethylenediamine-cobaltic ion undergoes partial hydrolysis as shown below.



This is supported by the conductivity measurement of the sodium salt, for which  $\lambda_\infty = 94$  (approx.), whereas  $\lambda_\infty$ -value for a uni-univalent sodium salt with a complex anion amounts to about 70 at 25° (Walden, *Das Leitvermögen der Lösungen*, 1924, 11, 189). The value of  $\Delta = \lambda_{1024} - \lambda_{32} = 21.4$  also points to the same conclusion.

#### EXPERIMENTAL.

##### *Sodium Dithiosulphato-diethylenediamine-cobaltate (trans).*

*Preparation.*—Finely-powdered cobalt acetate (10 g.) was treated with 55 c.c. of 10% ethylenediamine solution; the mixture was shaken till all the salt dissolved. A vigorous current of air was passed through the clear solution for 4–5 hours at a temperature of about 10°. Glacial acetic acid (2 c.c.) was afterwards added to the solution and the latter allowed to stand for some time. 50 G. of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , dissolved in the least quantity of water, were then added to the mixture, and this was left in a cool place for a day or two. Dark-green crystals, separated by this time, were drained and washed with a little cold water. The crude crystals, thus obtained, were purified by dissolving them in water by prolonged and repeated shaking, filtering off any insoluble residue, and then salting out the pure sodium salt by adding a saturated

solution of NaCl. Twice the volume of the saturated NaCl solution was added and the mixture shaken and allowed to stand for 2 hours. The dark-green shining leaflets separated, were drained washed at first with a little ice-cold water, then twice with 10 % alcohol and finally with absolute alcohol. (Found: N, 13·39, 13·58; S, 30·12, 30·02; Co, 13·98, 13·92; Na, 5·51, 5·47. Na- $[(S_2O_3)_2 \cdot Co \cdot En_2]$  requires N, 13·14; S, 30·04; Co, 13·86; Na, 5·4 per cent).

*Properties.*—The substance forms sparingly soluble, dark-green shining plates. The solution of the substance is greenish violet in colour, which becomes more violet on dilution. The latter turns red by the addition of alkalis. When warmed with ethylenediamine solution, triethylenediamine-cobaltic thiosulphate is formed. The substance is decomposed by acids with evolution of  $SO_2$  and S. Silver nitrate solution produces a greenish precipitate, which readily turns black.

*Equivalent conductivity at 25°.*

v ...	32	64	128	256	512	1024	2048 litres
$\lambda$ ...	64·8	69·3	71·9	76·3	80·6	86·2	94 mhos.

As already stated the conductivity values indicate partial hydrolysis of the salt in solution.

As the colour indicates, the substance is evidently a *trans* salt. But in solution, specially on dilution, the green colour gradually becomes more and more violet, showing that an equilibrium between the two modifications exists in solution. The transformation of the *trans* into *cis* variety is effected by the addition of alkalis, and the pure *cis* salt has been obtained, as described below, from an alkaline solution of the *trans* salt.

*Isomeric cis Sodium Salt.*

*Preparation.*—A solution of the green (*trans*) sodium salt was treated with a solution of chemically pure caustic soda (0·5 g.) in double-distilled alcohol. The mixture was kept over phosphorus pentoxide in an atmosphere free from  $CO_2$ . When the solution was reduced to a small bulk by evaporation and crystals of the red *cis* salt separated in quantities, the mixture was digested with absolute alcohol, allowed to stand for several hours in an atmosphere free from  $CO_2$ , and the supernatant clear solution was poured off from

the crystals. The washing was repeated till the alcoholic filtrate ceased to react alkaline. The substance was then dried over  $P_2O_5$ . (Found: N, 18.58; S, 80.14; Co, 18.90; Na, 5.45 per cent). The composition is identical with that for the *trans* salt.

*Properties.*—The red *cis* salt is extremely hygroscopic and highly soluble in water. The solution, when allowed to evaporate in air at the ordinary temperature, deposits green crystals of the *trans* salt. By repeated solution and evaporation it is completely converted into the green *trans* modification.

*Potassium Dithiosulphato-diethylenediamine-cobaltiate (trans).*

*Preparation.*—A saturated solution of the *trans* sodium salt was mixed with twice its volume of a saturated solution of KCl. The mixture was vigorously shaken and then allowed to stand for some time. The crystals, separated, were drained, washed at first with ice-cold water, then with dilute alcohol and finally with absolute alcohol. (Found: S, 27.08; Co, 12.34; K, 8.26.  $K[(S_2O_3)_2 \cdot Co \cdot En_2]$ ,  $2H_2O$  requires S, 26.8; Co, 12.34; K, 8.16 per cent).

The colour and other properties of the substance resemble those of the *trans* sodium salt. The *trans* salt can be converted into the *cis* variety as described in the case of sodium compound.

*Thallium Dithiosulphato-diethylenediamine-cobaltiate (trans).*

*Preparation.*—A solution of thallous nitrate was added, drop by drop, with shaking to a saturated solution of the *trans* sodium salt, when the *trans*-thallium salt was precipitated. Excess of thallous nitrate was avoided. The crystals were drained and washed as described in the previous cases. (Found: Co, 9.37; Tl, 82.68.  $Tl[(S_2O_3)_2 \cdot Co \cdot En_2]$ ,  $H_2O$  requires Co, 9.44; Tl, 82.68 per cent).

The substance forms dark-green, sparingly soluble, shining crystals.

## REVIEW.

**Donnees Numeriques sur les Colloides et L'Adsorption**, edited by G. Genin; Extrait des Volumes VIII (Annees 1927-1928) et IX (Annee 1929) of "Tables Annuelles de Constantes et Donnees Numeriques. Price 1£ 1s. Published by Gauthier-Villars Et Cie., Paris.

The compilation of the numerical data on Colloids and Adsorption has been made most carefully and will be very helpful to all who want to find out at a glance the numerical data relating to Colloids published during the period dealt with. In page 2011 reference is made to the peculiar difficulties relating to the absolute value of the data as Colloids but it is stated that "they certainly give an estimate of the order of the values, which is of the greatest interest for preliminary investigation and for laboratory research work. Finally, the examination of the numerical data leads to laws or at any rate to rules, of a general character. \* \* In compiling the Chapter on Colloids we have endeavoured to avoid as far as possible figures not sufficiently accurate and we give only deductions, resulting from their examination. These are the principal points which make us consider the Chapter on the Colloids a necessary part of the total program of the Annual Tables of Constants and Numerical Data". The publications on Colloids cover a very wide range and are to be found in every possible language. A systematic and critical collection of reliable data is obviously of the greatest advantage to all concerned. One feature which the writer has found very helpful is the reproduction of curves of the original papers. The volume gives an idea of the contributions of Indian workers and incidentally illustrates to what extent study of Colloids has been taken up in India. The publication is expected to find a place in all Institutions where researches on Colloids are being carried out.

J.N.M.

- **Donnees Numerique de Spectroscopie**. It is the reprint of the Section "Spectroscopy" of Vol. VIII (1928) and XI (1929) of the Annual Tables of Constants (A. T. C.) and Numerical data Chemical, Physical and Biological and Technical published under the patronage of the International Research Council, International

Union on Chemistry pure and applied and International Committee appointed by the Seventh Congress of Applied Chemistry. Published by Gauthier-Villars et Cie., Paris.

In Vol. VIII the data for the year 1927-1928 have been collected under the three heads viz., (1) Emission spectra (2) Absorption spectra and (3) Electro and Magneto optics, whereas in Vol. IX one finds data for 1929 and a new section "Scattering of light" has been added, dealing with the data on Raman-effect. The data have been classified by eminent French Scientists viz., Dr. Bruninghaus, Prof. Victor Henri, Dr. F. Wolfers and Dr. P. Anger.

One should not attempt to use these tables without first consulting the directions given at the beginning of each section. These are found to be clear, distinct and explicit. The practice of adopting French and English will be helpful to a large group of Indian students. In the section dealing with Emission spectra (L. Bruninghaus) one finds the atomic and molecular spectra classified according to the Periodic system instead of alphabetical order as adopted by Kayser in his *Handbuch der Spectroskopie*, a procedure that may be convenient for the chemists standpoint. The section on the Absorption spectra (Prof. Victor Henri) deals with the absorption spectra for ultra-violet and infra-red radiations for gases and for solutions. *Graphical tables* are given for liquids as well as for solutions where the spectral range is extended to visible region and also there is the other section dealing with the *Numerical values* of the absorption spectra for solids, liquids and solutions and here X-ray data for elements of different compounds are also supplied.

The section dealing with Electro and Magneto optic (F. Wolfers) has the collected data on the Zeeman-effect and Stark-effect, Electro-magnetic double refraction, Kerr-effect rotation and connected effects. "Scattering of light" section of Vol. IX (P. Anger) differs from the other sections in one aspect viz., that one does not find a sub-section dealing with the theoretical aspect.

As this book deals only with the data accumulated in the course of three years one may not be in a position to determine the critical nature of the different constants recorded here; but it may be also stated that such a Table would be very helpful to any laboratory where systematic researches are in progress.

**Technisch-Chemische Analyse** (Techno-chemical Analysis) By Ludwig Medicus. Third fully revised edition by Dr. H. Töpelmann, with an introduction by Prof. Dr. Wilh. Böttger, pp. VII + 170, with 28 figures. Published by Verlag von Theodr Steinkopff, Dresden and Leipzig, 1931.

The book is adapted to the requirements of the Applied Chemistry students for use as laboratory handbook. The subject matters have been dealt with in three different sections. In the first section the instruction begins with details of "sampling". This is followed by the descriptions of methods for the analysis of water, solid and liquid fuels, lubricants and gaseous mixtures.

The second section deals with colorimetry, the rapid methods of gravimetric analysis by L. W. Winkler, and gas-volumetry. The reviewer is, however, of opinion that Winkler's methods might have been omitted without losing anything and, in fact, could have been profitably substituted by many modern methods of analysis based on the use of special reagent, which are reliable and fairly rapid.

The third section gives instructions about the analysis of typical technically important metals, alloys and ores including the assaying of silver, methods for the technical analysis of clay, mortar, glass and manures are also dealt with in this section.

The book does not aim at comprehensiveness and is only short introduction to techno-chemical analysis. As such it will prove quite useful to the students of Applied Chemistry,

P. R.





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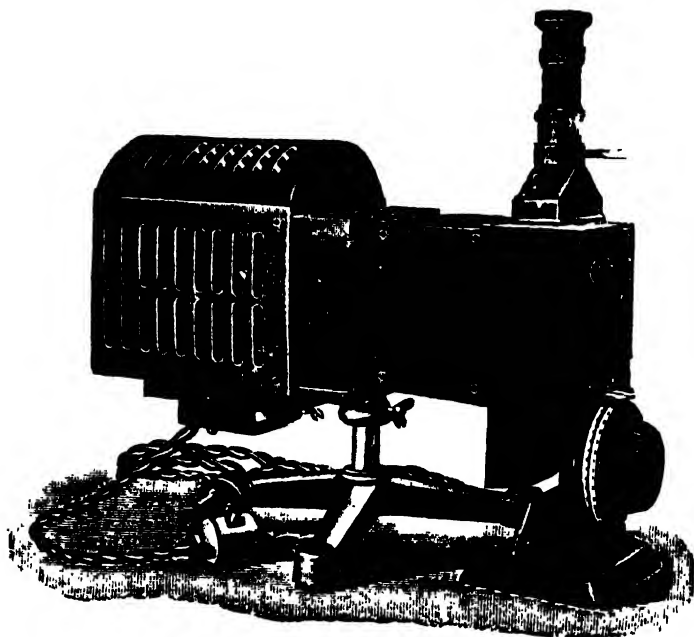
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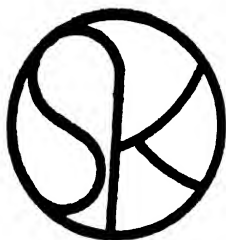
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This medal will be awarded from the Indian Chemical Society by Prof. Dr. S. S. Bhatnagar, to young Indian Chemist below thirty years of age for the best single original contribution published in the Journal of the Indian Chemical Society.

### **Rules.**

1. In commemoration of the Seventieth Birthday of Sir P. C. Rây a silver medal, awarded by Prof. S. S. Bhatnagar, shall be called "Sir Prafulla Chandra Rây 70th Birthday Medal."

2. The medal on one face shall bear the profile impression of Sir P. C. Rây, and on the other face— "Sir P. C. Rây 70th Birthday Commemoration Medal awarded to....."

3. The value of the medal will be Rs. 50.

4. The medal will be awarded annually for the best original paper (single and not joint) on any subject in Chemistry published in the Journal of the Indian Chemical Society only.

5. The competition for the medal shall be open to candidates whose age must not exceed thirty.

6. The candidates for the prize shall be required to submit an age certificate or corroboration of the same, confirmed by the Head of the department where they have worked.

7. The candidates, when communicating for publication in the Society's Journal, the paper intended for competition, must clearly make a statement to that effect.

8. The candidates for the medal shall submit their application not later than 31st October in every year, stating the title of their papers and the issue of the Journal in which they have been published.

9. No paper, which was submitted or has already been submitted for any other prizes or any examination, other than the M.A., or M.Sc., examination of the Indian Universities will be accepted for the present competition.

10. The merits of the papers shall be judged either by the Council of the Society or by the Board of Examiners, appointed by it, whose decision shall be considered final.

11. If in any year no prize is awarded by reason of no candidate having shown sufficient merit to entitle him to the prize or for any causes, the income of that year may be utilised in awarding a second prize in the next or in any subsequent year.

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Questions concerning documentation have of late assumed more and more importance. Scientific and technical documents increase on all sides in such numbers that it becomes more and more difficult to gather useful material for the benefit of inquirers. There are many bodies that deal permanently with the registering, classing and diffusion of such documents. Now the co-ordination of the respective activities of these institutions on an international basis has become necessary in order to permit them to carry on their work efficiently.

As regards the province of chemistry a step was taken in 1932, in the scientific and technical sphere, by the entry into activity of the INTERNATIONAL OFFICE OF CHEMISTRY, created by the international convention, and having its head quarters in Paris.

Its first act was the summoning of a Conference of Experts, which included the following personalities Messrs F. DONKER DUYVIS Member of the Council of Patents, The Hague; P. DUTOIT, Professor at the University of Lausanne; F. HABFR, Director of the Kaiser-Wilhelm Institute for Physikalische Chemie and Electrochemie, Berlin; E. HAUSER, Member of the Academy of Sciences, Madrid; Ch. MARIE, Secretary General of the Comité International des Tables Annuelles de Constantes, Paris; N. PARRAVANO, Member of the Academy of Italy, President of the Comitato Nazionale di Chimica, Rome; G. PENY, President of the Federation of Chemical Industries of Belgium, Brussels; J. C. PHILIP, Professor at the Imperial College of Science and Technology, London.

The work of this Conference of experts led to the adoption of a certain number of recommendations fixing the three principal tasks of the office.

I. To render accessible to all interested persons the already existing documentation, accumulated in the various centres, depots and collection.

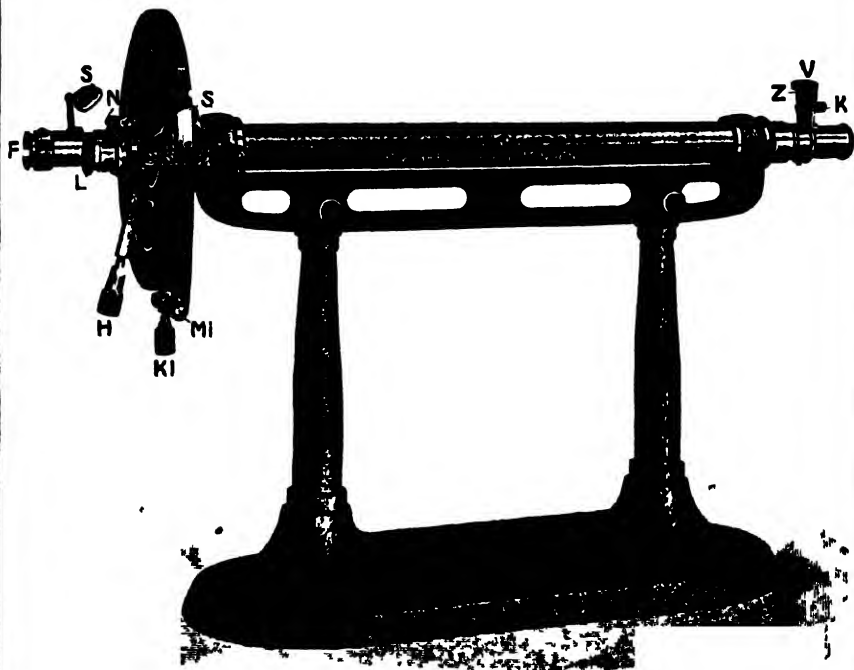
II. To guide the chemical documentation which is in course of production, in such a way as to facilitate its registering, filing and diffusion, by methods found to be the best.

III. To ensure co-ordination between the documentation relative to chemistry and that concerning other scientific knowledge in the field of international documentation.

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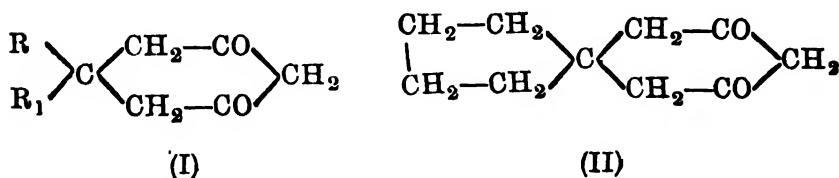
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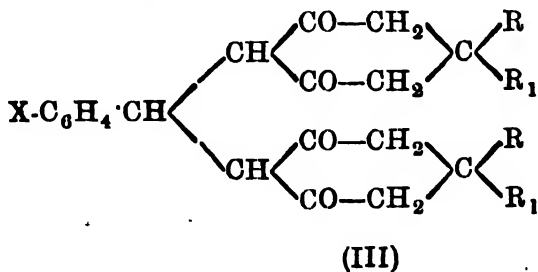
## Dihydroresorcinols. Part II. The Condensation of Aldehydes with *cyclopentane-spiro-cyclohexane-3:5-dione* and Dimethyldihydroresorcinol.

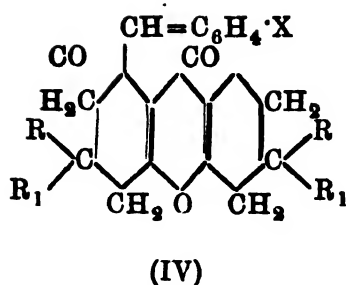
BY RANODHODJI DAJIBHAI DESAI.

It was the original intention of the author to prepare tetrahydrobenzopyranol dyes from various dihydroresorcinols of the general formula (I) where R, R<sub>1</sub> = H, alkyl, aryl, *cyclopentane* and *cyclohexane* radicals, with a view to studying their absorption spectra, in order to determine the effect exerted by alkyl and *gem*-dialkyl groups on the colour of these substances. Owing to difficulties met with in their utmost purification which was necessary for this type of work, the project had to be abandoned. In the meanwhile, a paper on the condensation of dimethyldihydroresorcinol with aromatic aldehydes was published by Chakravarti, Chattopadhyaya and Ghosh (*J. Ind. Inst. Sci.*, 1931, **14A** 141). This rendered much of the present author's work on dimethyldihydroresorcinol superfluous but the results obtained so far with *cyclopentanespirocyclohexane-3:5-dione* (II) are interesting enough for publication.



The action of benzaldehyde on dimethyldihydroresorcinol (I, R = R<sub>1</sub> = Me) and phenyldihydroresorcinol (I, R = H; R<sub>1</sub> = Ph) had already been studied by Vorländer (*Annalen*, 1899, **309**, 379) who showed that the primary products formed were benzalbisdihydroresorcinols (III, X = H) which were easily convertible by dehydration into the corresponding diketooctahydroxanthenes (IV, X = H).





The author observed that compound (III) was formed much more readily in presence of piperidine as a catalyst, whilst compound (IV) was exclusively formed with hydrogen chloride as a condensing agent. The behaviour of *cyclopentanespiro-cyclohexane-3:5-dione* was exactly similar, and benzaldehyde as well as salicylaldehyde reacted with the dione (II), at the ordinary temperature in presence of piperidine as a condensing agent, giving benzal-bis-*cyclopentanespiro-cyclohexane-3:5-dione* (III, X=H and  $\text{C} \begin{smallmatrix} \text{R} \\ \text{R}_1 \end{smallmatrix} = \text{C} < \text{C}_4\text{H}_8$ ) and salical-

bis-*cyclopentanespiro-cyclohexane-3:5-dione* (III, X=OH and  $\text{C} \begin{smallmatrix} \text{R} \\ \text{R}_1 \end{smallmatrix} = \text{C} < \text{C}_4\text{H}_8$ ). The dehydration of the benzal derivative by acetic anhydride, glacial acetic acid or dry hydrogen chloride gave 2-*spiro-cyclopentane-4:5-diketo-7-spiro-cyclopentane-9-phenyloctahydroxan*

thene (IV, X=H and  $\text{C} \begin{smallmatrix} \text{R} \\ \text{R}_1 \end{smallmatrix} = \text{C} < \text{C}_4\text{H}_8$ ). Under the same condi-

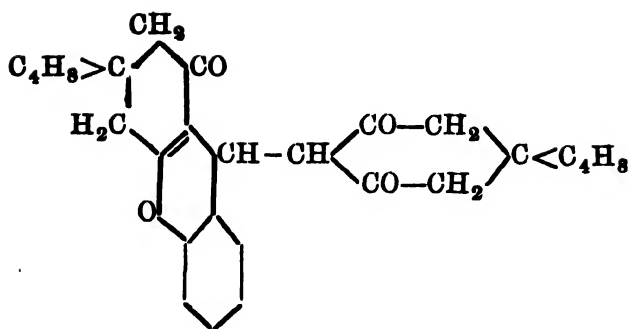
tions, the salical derivative could give rise either to 2-*spiro-cyclopentane-4:5-diketo-7-spiro-cyclopentane-9-o-hydroxyphenyloctahydroxan*

xanthene (IV, X=OH and  $\text{C} \begin{smallmatrix} \text{R} \\ \text{R}_1 \end{smallmatrix} = \text{C} < \text{C}_4\text{H}_8$ ) or to the pyran deriva-

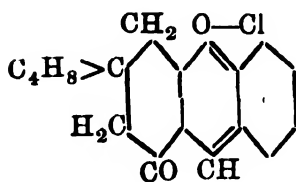
tive (V). But the product formed was the octahydroxanthene derivative, as acetyl salicylaldehyde condensed with the (II), giving acetyl-salicalbis-*cyclopentanespiro-cyclohexane-3:5-dione* (III, X=O·CO CH<sub>3</sub>

and  $\text{C} \begin{smallmatrix} \text{R} \\ \text{R}_1 \end{smallmatrix} = \text{C} < \text{C}_4\text{H}_8$ ) which could be dehydrated to the octa-

hydroxanthene derivative, identical with the one formed by the acetylation of 2-*spiro-cyclopentane-4:5-diketo-7-spiro-cyclopentane-9-o-hydroxyphenyloctahydroxanthene*,



(V)



(VI)

When salicylaldehyde was condensed with the dione (II) in presence of dry hydrogen chloride, a scarlet compound was formed and this was found to be 2-*spiro-cyclopentane-4-ketotetrahydrobenzopyranol-anhydrochloride* (VI). Other dihydroresorcinols behaved similarly and this reaction was studied with dimethyldihydroresorcinol, phenyldihydroresorcinol and *cyclohexanespiro-cyclohexane-3:5-dione*. Thus these dihydroresorcinols behaved like  $\alpha$ -hydrindone and diketohydrindene from which pyranol dyes have already been prepared (Perkin, Robinson and Turner, *J. Chem. Soc.*, 1908, 93, 1085; Sastry and Ghosh, *ibid.*, 1915, 107, 1442).

The formation of the anhydrochloride (VI) must have involved the intermediate formation of *salicylidenecyclopentane-spiro-cyclohexane-3:5-dione* but attempts to prepare it from the aldehyde and the dione (II) by condensing them with or without the alkaline as well as acid condensing agents failed. The hydrolysis of the anhydrochloride (VI) with strong caustic potash was also tried, but the resulting product was the anhydro base (VI, OH in place of Cl) which resisted the action of the alkali. Similarly the dimethyl analogue of the anhydro base was unaffected by the action of caustic alkali. The stability of these anhydro bases could only be accounted for by the presence of a *cyclopentane* nucleus and a *gem*-dimethyl group. That this sort of stabilising effect is exerted by the

*gem*-dimethyl group has its parallel in the observation of Vorländer (*Annalen*, 1896, 294, 275) who failed to hydrolyse dimethyldihydroresorcinol to  $\beta\beta$ -dimethyl- $\gamma$ -acetobutyric acid while dihydroresorcinol readily underwent hydrolysis to  $\gamma$ -acetobutyric acid. <sup>1</sup>

By condensing salicylaldehyde with dimethyldihydroresorcinol in presence of caustic potash, Chakravarti, Chattopadhyaya and Ghosh (*loc. cit.*) obtained a product melting at 206°, and having the empirical formula  $C_{23}H_{26}O_4$ . These authors formulated it as *o*-hydroxybenzaldimethyldihydroresorcinol anhydride [ $V$ ,  $C < C_4H_8 = C(CH_3)_2$ ]. In assigning the pyran structure, the arguments advanced were neither cogent nor conclusive. The present author is of opinion that the above compound can best be formulated as the xanthene derivative, and should be called 2:2:7:7-tetramethyl-4:5-diketo-9-*o*-hydroxyphenyloctahydroxanthene (IV,  $X = OH$ ,  $R = R_1 = CH_3$ ). This constitution is supported by the fact that the acetyl derivative of this compound is identical with the dehydration product of acetylsalicalbisdimethyldihydroresorcinol (III,  $X = O \cdot CO \cdot CH_3$ ;  $R = R_1 = CH_3$ ) which is formed by the condensation of acetylsalicylaldehyde with dimethyldihydroresorcinol in presence of piperidine at ordinary temperature; also its methylated product is identical with the dehydrated product of *o*-methoxybenzalbisdimethyldihydroresorcinol (III,  $X = OCH_3$ ;  $R = R_1 = CH_3$ ) which is obtained by the action of *o*-methoxybenzaldehyde on dimethyldihydroresorcinol.

#### EXPERIMENTAL.

*cyclo*Pentanespiro-*cyclo*hexane-3:5-dione was prepared by the method of Norris and Thorpe (*J. Chem. Soc.*, 1921, 119, 1205). When its alcoholic solution was treated with an excess of 40% formaldehyde solution at ordinary temperature methylenebis*cyclo*-pentanespiro*cyclo*hexane-3:5-dione was immediately precipitated, m. p. 165°.

2-spiro-*cyclo*Pentane-4:5-diketo-7-spiro-*cyclo*pentane-octahydroxanthene.—The above methylene derivative (1 g.) was heated with acetic anhydride (5 c. c.) on a free flame for 3 hours and the excess of the anhydride decomposed by adding water. The precipitated solid crystallised from alcohol as tiny, white needles, m. p. 180-81°.

(Found: C, 77.1; H, 8.1.  $C_{21}H_{26}O_3$  requires C, 77.3; H, 8.0 per cent).

*Benzal-bis-cyclopentanespiro-cyclohexane-3:5-dione* [III, X = H,  $C \begin{smallmatrix} \nearrow R \\ \searrow R_1 \end{smallmatrix} = C < C_4H_8$ ].—A mixture of benzaldehyde (2 g.), cyclopentane-spiro-cyclohexane-3:5-dione (3.5 g.), dry benzene (25 c. c.) and piperidine (4 drops) was kept at the ordinary temperature for 12 hours. The residue left after the removal of benzene under suction crystallised from dilute alcohol as white plates or needles, m. p. 167°. Its alcoholic solution gives a reddish-brown colouration with ferric chloride solution. (Found: C, 77.0; H, 7.8.  $C_{27}H_{32}O_4$  requires C, 77.1; H, 7.6 per cent).

*2-spiro-cyclopentane-4:5-diketo-7-spiro-cyclopentane-9-phenyloctahydroxanthene* (IV, X = H,  $C(RR_1) = C < C_4H_8$ ).—When the above compound (1 g.) was heated with acetic anhydride (5 c. c.) on a free flame for 15-20 minutes and the excess of the anhydride decomposed with water, a solid was precipitated. This crystallised from alcohol as compact cubes, m. p. 185-86°. Its alcoholic solution does not give colouration with ferric chloride solution. (Found: C, 80.4; H, 7.6.  $C_{27}H_{30}O_3$  requires C, 80.6; H, 7.6 per cent).

*Salical-bis-cyclopentanespiro-cyclohexane-3:5-dione* [III, X = OH,  $C(RR_1) = C < C_4H_8$ ].—A mixture of salicylaldehyde (2 g.), cyclopentanespiro-cyclohexane-3:5 dione (3.4 g.), dry benzene (20 c. c.) and piperidine (4 drops) was kept at the room temperature for 12 hours. The solid that separated out crystallised from alcohol as white plates, m. p. 208-09°. It is readily soluble in dilute caustic alkali and its alcoholic solution gives reddish violet colouration with ferric chloride. (Found: C, 74.2; H, 7.4.  $C_{27}H_{32}O_5$  requires C, 74.3; H, 7.3 per cent).

*2-spiro-cyclopentane-4:5-diketo-7-spiro-cyclopentane-9-o-hydroxy phenyloctahydroxanthene* (IV, X = OH,  $C(RR_1) = C < C_4H_8$ ).—The above compound (1 g.) was boiled with glacial acetic acid (15 c. c.) for 4 hours. On dilution, white needles melting to a red liquid at 191° were obtained. It is soluble in alkali and its alcoholic solution gives a violet colouration with ferric chloride. The same

substance could also be prepared by saturating the absolute alcoholic solution of the foregoing salical derivative with dry hydrogen chloride at  $0^{\circ}$  and keeping for 12 hours. (Found: C, 77.8; H, 7.2.  $C_{27}H_{30}O_4$  requires C, 77.5; H, 7.2 per cent).

The *acetyl* derivative was prepared by heating either the salical derivative or the xanthene derivative with acetic anhydride for  $\frac{1}{2}$  hour on a sand-bath. The solid left after decomposing the excess of the anhydride crystallised from dilute alcohol as prismatic needles, m. p.  $181-82^{\circ}$ . (Found: C, 75.6; H, 7.1.  $C_{29}H_{32}O_5$  requires C, 75.6; H, 7.0 per cent).

The *benzoyl* derivative was prepared by treating the pyridine solution of the xanthene derivative with benzoyl chloride. On dilution with water an oil, which slowly solidified, was obtained. It crystallised from alcohol in plates, m. p.  $137^{\circ}$ . (Found: C, 78.1; H, 6.6.  $C_{34}H_{34}O_5$  requires C, 78.2; H, 6.5 per cent).

*Acetylsalicalbiscyclopentanespiro-cyclohexane-3:5-dione* [III,  $X = O \cdot COCH_3$ ,  $C(RR_1) = C < C_4H_8$ ].—This was prepared, like the benzal analogue, by using acetylsalicylaldehyde and crystallised from dilute alcohol in white needles, m. p.  $206^{\circ}$ . Its mixed m. p. with salical-bis-cyclopentanespiro-cyclohexane-3:5-dione was  $180-84^{\circ}$ , and the alcoholic solution gives a reddish brown colouration with ferric chloride. (Found: C, 72.5; H, 7.2.  $C_{29}H_{34}O_6$  requires C, 72.8; H, 7.1 per cent).

When this substance was boiled with acetic anhydride for 15 minutes or glacial acetic acid for 4 hours, the resulting product was identified as the acetyl-derivative of the diketooctahydroxanthene derivative by the m. p. and mixed m. p.

*2-spiro-cyclopentane-4-diketotetrahydrobenzopyranol anhydrochloride*. (VI).—A solution of cyclopentane-spiro-cyclohexane-3:5-dione (1 g.) and salicylaldehyde (7 g.) in absolute methyl alcohol (10 c. c.) was saturated with a rapid current of dry hydrogen chloride at  $0^{\circ}$ . The mixture became dark red and viscous and on keeping overnight scarlet crystals were deposited. These were filtered off, and washed on the filter paper with methyl alcohol saturated with dry hydrogen chloride. It is sparingly soluble in most of the organic solvents and charred without melting at  $300^{\circ}$ . The sample for analysis was dried in a vacuum over caustic potash. (Found: C, 70.6; H, 6.0; Cl, 11.6.  $C_{17}H_{17}O_2Cl$  requires C, 70.7; H, 5.9; Cl, 12.8 per cent).

The *anhydro base* was prepared by adding sodium acetate solution to the warm solution of the anhydro-chloride in a large excess of ethyl alcohol. The pink powder that was precipitated was filtered off and washed alternately with water, alcohol and ether. It is sparingly soluble in the usual organic solvents, and does not melt below 300°. It was recovered unchanged after heating with a concentrated solution of alcoholic caustic potash, and the anhydro-chloride was formed on adding it to methyl alcohol saturated with dry hydrogen chloride. (Found: C, 75.4; H, 6.8.  $C_{17}H_{18}O_3$  requires C, 75.6; H, 6.7 per cent).

*Dimethyldihydroresorcinol* was prepared by the method of Vorländer (*Annalen*, 1897, 294, 253). The hydrolysis of the dione ester was carried out by alcoholic potash, as this required only 3 to 4 hours, yield 80%.

*Benzalbisdimethyldihydroresorcinol* was prepared from benzaldehyde and dimethyldihydroresorcinol, like the *cyclopentane* analogue. It crystallises from alcohol as white plates, m. p. 196-97° and gives violet colouration with ferric chloride. The m. p. given by Vorländer (*loc. cit.*) is 193°, while that given by Chakravarti, Chattopadhyaya and Ghosh (*loc. cit.*) is 175-76°. (Found: C, 74.9; H, 7.9. Calc: C, 75.0; H, 7.6 per cent).

*2:2:7:7-Tetramethyl-4:5-diketo-9-phenyloctahydrozanthene* was prepared from the above substance by dehydrating it with glacial acetic acid, acetic anhydride or dry hydrogen chloride and crystallised from alcohol as white needles, m.p. 202°. The m.p. given by Chakravarti, Chattopadhyaya and Ghosh (*loc. cit.*) is 193°. (Found: C, 78.9; H, 7.5. Calc: C, 78.8; H, 7.4 per cent).

The *phenylhydrazone* prepared by heating the substance with an equivalent amount of phenylhydrazine in glacial acetic acid solution for 1 hour on a water-bath crystallised from acetic acid in yellow needles, m.p. 266-67° (decomp.). (Found: C, 78.9; H, 7.4.  $C_{29}H_{32}O_2N_2$  requires C, 79.1; H, 7.3 per cent).

*Salicalbisdimethyldihydroresorcinol* was prepared from salicylaldehyde and dimethyldihydroresorcinol like its benzal analogue and crystallised from dilute alcohol in white plates, m.p. 184°. (Found: C, 71.7; H, 7.5.  $C_{23}H_{28}O_5$  requires C, 71.9; H, 7.3 per cent).

When this was heated with glacial acetic acid for 4 hours, *2:2:7:7-tetramethyl-4:5-diketo-9-o-hydroxyphenyl-octahydrozanthene* (IV, X=OH, R=R<sub>1</sub>=CH<sub>3</sub>), which crystallised from alcohol in white

rhombohedra, m.p.  $209-10^{\circ}$  was formed. The same substance is also formed by condensing salicylaldehyde with dimethyldihydroresorcinol in presence of caustic potash. (cf. Chakravarti, Chattopadhyaya and Ghosh, *loc. cit.*). (Found: C, 75.8; H, 7.8. Calc: C, 75.4; H, 7.1 per cent).

The *acetyl* derivative, prepared by heating the above compound with acetic anhydride, crystallised from dilute alcohol in prismatic needles, m.p.  $190-91^{\circ}$ . (Found: C, 73.3; H, 6.9. Calc: C, 73.5; H, 6.8 per cent).

The *benzoyl* derivative crystallised from dilute alcohol in clusters of white, tiny needles, m.p.  $154-55^{\circ}$ . (Found: C, 76.7; H, 6.6. Calc: C, 76.6; H, 6.4 per cent).

The *phenylhydrazone* crystallised from alcohol in colourless needles, m.p.  $235^{\circ}$ . (Found: C, 76.1; H, 7.3.  $C_{29}H_{32}O_2N_2$  requires C, 76.3; H, 7.0 per cent).

The *methyl ether* (IV,  $X=OCH_3$ ;  $R=R_1=CH_3$ ) prepared by heating the substance (0.5 g.) with methyl iodide (2. c.c.) at  $100^{\circ}$  for 12 hours, crystallised from dilute alcohol in white needles, m.p.  $180^{\circ}$ . (Found: C, 75.6; H, 7.5.  $C_{24}H_{28}O_4$  requires C, 75.8; H, 7.4 per cent).

*Acetylsalicaldimethyldihydroresorcinol* (III,  $X=O\cdot COCH_3$ ;  $R=R_1=CH_3$ ).—This was prepared, like the cyclopentane analogue, from acetylsalicylaldehyde and dimethyldihydroresorcinol and crystallised from dilute alcohol in white needles, m.p.  $200-01^{\circ}$ . Its alcoholic solution gives colouration with ferric chloride. (Found: C, 71.1; H, 6.9.  $C_{26}H_{30}O_6$  requires C, 71.2; H, 6.8 per cent).

When this substance was dehydrated either by heating with acetic anhydride (30 min.) or glacial acetic acid (4 hours) or saturating its absolute alcoholic solution with hydrogen chloride, the resulting product was identified as the acetyl derivative of 2:2:7:7-tetramethyl-4:5-diketo-9-o-hydroxyphenyl-octahydroxanthene by m.p. and mixed m.p.

*o-Methoxybenzalbisdimethyldihydroresorcinol* (III,  $X=OCH_3$ ,  $R=R_1=CH_3$ ).—This was prepared like the preceding compound by using *o*-methoxybenzaldehyde and crystallised from dilute alcohol in white, tiny needles, m.p.  $184^{\circ}$ . Its m.p. was depressed to  $156^{\circ}$  by admixture with a specimen of salicalbisdimethyldihydroresorcinol which had also the same melting point. Its alcoholic solution gives violet-blue colouration with ferric chloride. (Found: C, 72.3; H, 7.7.  $C_{24}H_{30}O_5$  requires C, 72.4; H, 7.5 per cent). When



it was dehydrated by the usual methods, the resulting product was identified as the methyl ether of 2:2:7:7-tetramethyl-4:5-diketo-9-o. hydroxyphenyloctahydroxanthene by m.p. and mixed m. p.

Most of the work described in this paper was carried out at the Imperial College of Science and Technology, London, and the author wishes to thank Prof. J. F. Thorpe C.B.E., F.R.S. for his kind interest and encouragement, the University of Bombay for the award of a Scholarship, and the Chemical Society, London, for a grant which partly defrayed the cost. I am also indebted to Prof. H. K. Sen of the Calcutta University for some helpful criticism.

THE CHEMISTRY DEPARTMENT,  
MUSLIM UNIVERSITY,  
ALIGARH.

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# **Preliminary Chemical Examination of the Bark of *Holarrhena Antidysenterica*.**

BY SALIMUZZAMAN SIDDIQUI AND P. PARAMESWAREN PILLAY.

In a detailed communication (*J. Indian Chem. Soc.*, 1932, 9, 558) on the isolation and characterisation of three new bases from the Indian *Holarrhena* we have already described the method employed for the extraction of the alkaloid, which gives more than twice the yield of total alkaloid, so far obtained by any of the previous authors and conessine in a yield about four times as high as any, referred to in literature. Payman (*J. Chem. Soc.*, 1919, 115, 163), however, had got 0.25% conessine from *Holarrhena Congolensis* Stapf, and Giemsa and Halberkann (*Arch. Pharm.*, 1918, 256, 201) 0.7% conessine and 1.7% total alkaloid from *Holarrhena Africana*. As the different authors have used very varying methods for the extraction of the alkaloids, it appeared to us of great interest to compare the yield of alkaloids obtained by these different methods from the same sample of bark to test and establish the value of the method evolved by us. Also we found it desirable to make a cursory examination of the non-alkaloidal constituents.

As a result of these investigations we have found out that the ammonia-alcohol-ether mixture employed by us is the best means of extracting the alkaloids, which occur in the plant body as tannates, which are very difficultly soluble in alcohol or acidulated alcohol or water, but are easily liberated from their tannic acid salts by alkalis. The physiological action of the crude bark and its extract in the treatment of intestinal troubles, may also be due to this fact as the tannates of the alkaloids would remain undissolved in the acid juices of the stomach and pass on to the seat of disease in the intestines.

Besides isolating a tannate of the alkaloids we have detected the presence of linoleic acid as a component of the fatty matter and isolated in quite a large yield liquid sterols and a crystalline sterol which we have identified to be lupeol.

## **EXPERIMENTAL.**

Different methods of extraction of the alkaloids were tried with the same sample of powdered bark and the results obtained are given in the following table. In each case the alkaloid was finally purified by dissolving out with ether containing 10% alcohol. The number of percolations and the quantity of solvent used in each case was the same.

Extraction media.	Mode of separating the alkaloids.	Yield.	Remarks.
1. Cold alcoholic percolation.	Alcohol removed under reduced pressure and alkaloids extracted from residue.	1.05%	Method used by Ghosh & Ghosh ( <i>J. Indian Chem. Soc.</i> , 1928, 5, 477), yield 1.28% in assay and 0.7% in large extraction.
2. Same.	Solvent distilled off under ordinary pressure.	0.5	There was some resinous basic residue insoluble in ether-alcohol.
3. Soxhleted for 18 hrs. with alcohol.	Solvent distilled off under ordinary pressure.	1.4	Basic resinous residue, insoluble in alcohol and ether.
4. Percolated with ether containing 10% of alcohol and 2% liq. ammonia.	Alkaloids extracted with dilute acetic acid.	1.7	
5. Alcohol containing 10% liq. ammonia.	Made faintly acidic with acetic acid; alcohol distilled under reduced pressure.	1.75	
6. Treated with 10% alc. KOH then percolated with ether containing 10% alcohol.	Made faintly acidic with acetic acid, solvent distilled off, finally under reduced pressure.	1.53	
7. Percolation with very dilute HCl	Made faintly alkaline with $\text{Ca}(\text{OH})_2$ . Extracted the dried precipitate with petrol and the filtrate with ether.	0.8 yielded crude conessine (m.p. 122°) 0.3%	Voluminous brown ppt. Giemsa & Halberkann ( <i>loc. cit.</i> ) got 1.7% by this method from H. African raw.

The best method of extraction was found to be method (4) followed by a further series of extractions using 80 parts ether and 15 parts alcohol mixed with 10 parts of liquor ammonia. By this method a total yield of 2.1% was obtained.

*Insoluble tannate of the alkaloids.*—500 G. of the drug, percolated with alcohol, yielded 22 g. of extractive on removal of the solvent under reduced pressure. To this 100 c.c. of water were added and the neutral products extracted off with ether. To the aqueous filtrate drops of sodium hydroxide solution were carefully added until the solution was just alkaline, when a rose coloured precipitate of the tannate was formed (7.5 g.) which was filtered off and dried. It was found to be insoluble in water or cold dilute mineral acids, partially soluble in alcohol and soluble in dilute acetic acid. The alkalis, as well as the boiling dilute mineral acids decompose it. Its solution in alcohol is coloured green by ferric chloride. A trace of alkali changes it to violet. On decomposition with caustic soda it yielded about 20% by weight of alkaloids, traces of a resinous acid

and an acid filtrate which gave the usual colour reactions of a tannin of the phlobaphene group.

### *The Neutral Products.*

*Lupeol*.—The ether soluble neutral products left after the extraction of the alkaloids from the ether-alcohol-ammonia percolates of the drug (yield 2% on weight of dry bark) were saponified in the usual manner, yielding 1.2% of unsaponified matter and 0.5% of fatty acids. The unsaponifiable matter yielded 0.2% of crude lupeol directly out of alcohol and further 0.4% of it through acetylation of the mother liquors. After repeated recrystallisation from alcohol and ethyl acetate, pure lupeol was obtained in star shaped aggregates of needles, m.p. 213-14°. In a 2.06% chloroform solution it showed a rotation of  $D^{35} = +27.4^\circ$ . The melting point given for lupeol is 210° and the rotation noted for it by previous authors is variously given from +25.95° to +27.4°. (Found: C, 84.3; H, 11.8.  $C_{31}H_{50}O$  requires C, 84.9; H, 11.8 per cent). Lupeol acetate prepared in the usual manner, melted at 214°. (Found: C, 82.1; H, 11.0.  $C_{33}H_{52}O_2$  requires C, 82.5; H, 10.8 per cent). Lupeol benzoate melts at 266°.

*Uncrystallisable sterol*.—The unsaponifiable matter further yielded a brownish glassy solid which melted to a viscous liquid between 25-30° (0.3%). It could not be distilled at a pressure of 5 mm. (showing thereby that high aliphatic alcohols are absent), but gave all the usual colour reactions of sterols with Burchard Lieberman's, Salrowski's and Moleschott's tests and appeared to be an uncrystallisable sterol.

*Fatty acids*.—(Yield 0.5% on wt. of the bark). These were separated by the lead method into solid acids (0.13%), m. p. 58-70° and liquid acids (0.35%). The latter on bromination in a mixture of glacial acetic acid and ether yielded a small quantity of an insoluble bromide, m.p. 174-76°, which appeared to be linolenic acid hexabromide. About half of the remaining bromides, when recovered, were found to be soluble in petrol and the other half insoluble. The liquid acids, therefore, appeared to be a nearly equal mixture of oleic and linoleic acids with a trace of linolenic acid and were not further investigated.



# Behaviour of Nitrophenols with *p*-Toluenesulphonyl Chloride. Part IV.

By SHIAM SUNDAR JOSHI.

While studying the behaviour of *p*-toluenesulphonyl chloride with dinitrophenols in presence of diethylaniline (Sane and Joshi, *J. Chem. Soc.*, 1924, 125, 2481; *J. Indian Chem. Soc.*, 1928, 5, 299; 1932, 9, 59), it was usually observed that when there were two nitro groups either in both the *ortho* positions, or the *ortho* and the *para* positions with respect to a hydroxyl group, the hydroxyl group was replaced by a chlorine atom. However, when there was a methyl group in the *meta* position with respect to the hydroxyl in the compounds previously studied namely, 3:5-dimethyl-2:4-dinitrophenol under similar experimental conditions no replacement took place, only esters were formed. This influence of a *meta* situated methyl group on the replaceability of a hydroxyl by a chlorine atom is not the same even in the case of similar dinitrophenols; thus in 3-methyl-2-bromo-4:6-dinitrophenol the hydroxyl group is replaced, as usual, by a chlorine atom but in 3-methyl-2-iodo-4:6-dinitrophenol no replacement could be effected, only an ester is obtained. Like the esters of other dinitrophenols, this ester is quite reactive and easily yields derivatives with ammonia and aniline.

It may here be noted that a similar influence of a *meta* situated methyl group was also observed while studying the additive compounds of dinitrohalogenobenzenes with pyridine. 3-Chloro-4:6-dinitrotoluene, 3-bromo-4:6-dinitrotoluene and 3-chloro-2-bromo-4:6-dinitrotoluene did not yield additive compounds with pyridine, though other 2:4- and 2:6-dinitrohalogenobenzenes did so readily (Joshi, *J. Chem. Soc.*, 1933, 313).

## EXPERIMENTAL.

2-Iodo-4:6-dinitro-*m*-cresol was formed on treating a hot alcoholic solution of 4:6-dinitro-*m*-cresol (2 g.) first with iodine (2.6 g.) and then with mercuric oxide in small amounts at a time; the cresol was obtained from it by filtering the hot liquid, removing the alcohol and extracting the residue with benzene. It is crystallised from dilute acetic acid in yellow crystals, m. p. 93°. (Found: N, 8.65.  $C_7H_5O_5N_2I$  requires N, 8.64 per cent).

2-Iodo-4:6-dinitro-*m*-cresyl-*p*-toluenesulphonate was obtained by heating together on a boiling water-bath for 4 hours 2-iodo-

4:6-dinitro-*m*-cresol (8 g.), *p*-toluenesulphonyl chloride (2 g.) and diethylaniline (8 c.c.). The ester is slightly soluble in alcohol, more easily in acetone. It crystallises from a mixture of alcohol and acetone in colourless crystals, m.p. 136-37°, yield 4 g. (Found: S, 6.54.  $C_{14}H_{11}O_7N_2IS$  requires S, 6.70 per cent).

The same ester was obtained by condensing the cresol with toluenesulphonyl chloride in presence of sodium carbonate solution.

2-Iodo-4:6-dinitro-*m*-toluidine results by passing dry ammonia through a solution of 2-iodo-4:6-dinitro-*m*-cresyl-*p*-toluene sulphonate in an excess of alcohol for 45 minutes. It dissolves easily in the common organic solvents and crystallises from alcohol in yellow crystals, m. p. 97°, yield 2.8 g. (Found: N, 13.17.  $C_7H_6O_4N_3I$  requires N, 13.0 per cent).

3-Methyl-2-iodo-4:6-dinitrodiphenylamine was obtained when 2-iodo-4:6-dinitro-*m*-cresyl-*p*-toluenesulphonate (5 g.) and aniline (10 c.c.) were kept on a boiling water bath for  $\frac{1}{2}$  hour. It crystallises from slightly diluted acetic acid in yellow crystals, m. p. 143-44°, yield 90%. (Found: N, 10.25.  $C_{13}H_{10}O_4N_3I$  requires N, 10.53 per cent).

2-Bromo-4:6-dinitro-*m*-cresyl-*p*-toluenesulphonate was obtained by boiling in water 2-bromo-4:6-dinitro-*m*-cresol (2.8 g.) and *p*-toluenesulphonyl chloride (2.1 g.) with small amounts of sodium carbonate (1.2 g.) at a time. The ester crystallises from acetone and alcohol in colourless crystals, m. p. 141°, yield 3 g. (Found: S, 7.19.  $C_{14}H_{11}O_7N_2BrS$  requires S, 7.42 per cent).

2-Bromo-4:6-dinitro-*m*-toluidine was obtained by passing dry ammonia through a boiling alcoholic solution of 3-chloro-2-bromo-4:6-dinitrotoluene (2.8 g.). It dissolves easily in common organic solvents. It crystallises from alcohol and also from dilute acetic acid in yellow crystals, m. p. 80°, yield 2 g. (Found: N, 15.02.  $C_7H_6O_4N_3Br$  requires N, 15.22 per cent).

3-Methyl-2-bromo-4:6-dinitrodiphenylamine was obtained by boiling a solution of 3-chloro-2-bromo-4:6-dinitrotoluene (1.5 g.) in alcohol, aniline (1 g.) and sodium acetate (1 g.) for  $\frac{1}{2}$  hour. The compound dissolves easily in acetic acid and slightly in alcohol. It crystallises from alcohol in yellow crystals, m. p. 128°, yield 1.6 g. (Found: N, 11.81.  $C_{13}H_{10}O_4N_3Br$  requires N, 11.93 per cent).



# Dyes Derived from Acenaphthenequinone. Part IV. Azines and Indigoid Vat Dyes.

By SISIR KUMAR GUHA.

In continuation of the papers in this series (Sircar and Guha, *J. Chem. Soc.*, 1924, 125, 335 ; Guha, *ibid.*, 1931, 582 ; Guha, *J. Indian Chem. Soc.*, 1932, 9, 423), this investigation was undertaken with a view to study if in the acenaphthenequinone series, azines could be prepared having acenaphthene nucleus on both the sides of the azine ring and if such arrangement, which will at the same time increase the complexity of the molecule, has got any effect in deepening the colours of the resulting azines.

This led the author to condense acenaphthenequinone and its various derivatives with 2:3-diaminoacenaphthene (Sachs and Mosebach, *Ber.*, 1911, 44, 2852) and the compounds obtained are acenaphtheno-, acenaphtheno-3-chloro-, acenaphtheno-3-bromo-, acenaphtheno-1-methoxy-, and acenaphtheno-3:4-dinitroacenaphthazines. These azines are yellow, brownish yellow and chocolate coloured crystalline substances and they dissolve in concentrated sulphuric acid producing deep violet, violet blue and deep green solutions from which water reprecipitates the substances unchanged, quite suitable for dyeing on wool from an acid bath. The dyed shades on wool are yellow and chocolate. The yellow shade obtained on wool from acenaphtheno-acenaphthazine is in no way inferior to the same shade of the corresponding phenanthraquinone derivative (Sachs and Mosebach, *loc. cit.*). It is also observed that the introduction of NO<sub>2</sub> group in the molecule of acenaphtheno-acenaphthazine distinctly deepens the colour from the yellow to chocolate (*cf.* Fluoreno-acenaphthazines, Dutt, *Ber.*, 1932, 65, 1798).

$\beta$ -Methoxyacenaphthenequinone and 1-methoxyacenaphthaphenazine melt at 221-22° and 187-88° respectively. Staudenger, Goldstein and Schlenker (*Helv. Chim. Acta*, 1921, 4, 342) record m. p. 215-16° and 182-85° respectively.

Lastly further studies in indigoid vat dyes in the Ciba Scarlet G. series (*cf.* Guha, *J. Indian Chem. Soc.*, *loc. cit.*) have been made by condensing 5-methyl-8-hydroxythionaphthene (Auwers and Arndt, *Ber.*, 1909, 42, 541) with acenaphthenequinone, its chloro, bromo, and methoxy derivatives only ; the first three indigoid dyes easily

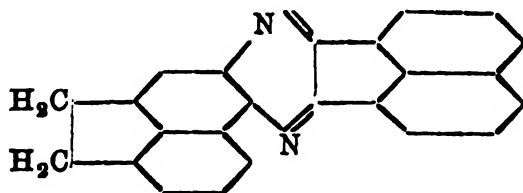
yield with alkaline hydrosulphite soluble blue vats from which the original scarlet products are regenerated on cotton by atmospheric oxygen. But in the case of the last named compound, the methoxy derivative, great difficulty was experienced in making use of it in the vat (*cf.* 2-thionaphthene-8'-(1'-methoxy) acenaphthylene-indigo, Staudinger and others, *loc. cit.*). The blue vat obtained in this case also on cotton turned only pink by treatment with air. Repeated attempts to secure the desired deep red shade on cotton were, however, unsuccessful. All the four substances dissolve in strong sulphuric acid producing deep green solutions from which the vat dyes are reprecipitated unchanged by the addition of water and as such each of them is suitable for dyeing on wool from an acid bath. The scarlet red shade obtained on cotton as well as on wool from the indigoid derivatives mentioned above are deeper than those of Ciba Scarlet G (Bezdzik and Friedlander, *Monatsch.*, 1908, 29, 306; and E. P. 844/1908) and its halogen derivatives (Guha, *loc. cit.*).

The azines, excepting the dinitro compound which does not melt but sublimes and the indigoid vat dyes on heating above their melting points volatilise unchanged producing coloured vapours of the individual product and deposit the dyes as pure compounds.

Further work in indigoid vat dyes in the acenaphthenequinone series is in progress.

#### EXPERIMENTAL.

##### *Acenaphthenoacenaphthazine.*



This compound separated immediately as rectangular brownish-yellow crystals on heating acenaphthenequinone (0.278 g.) and 2:8-diaminoacenaphthene (0.276 g) in 22 c.c. of boiling glacial acetic acid. It was first boiled with alcohol in which it was only sparingly soluble and then repeatedly extracted with acetic acid. The precipitate, obtained by the addition of water to the combined extract, was crystallised from amyl alcohol in elongated diamond shaped yellow crystals not melting below 815°. It is soluble in benzene,

xylene, pyridine or amyl alcohol, moderately soluble in acetic acid, sparingly soluble in ligroin, ethyl acetate and acetone. It dissolves in strong sulphuric acid with a deep violet colour and dyes wool in yellow shades from an acid bath. (Found: N, 8.81.  $C_{24}H_{14}N_2$  requires N, 8.48 per cent).

*Acenaphtheno-3-chloroacenaphthazine*.—This compound was prepared similarly from 3-chloroacenaphthenequinone (0.216 g.) and 2:3-diaminoacenaphthene (0.184 g.) in 25 c.c. of boiling glacial acetic acid and after being boiled with alcohol, it crystallised from pyridine in glistening yellow plates, not melting below  $815^\circ$ . It is soluble in nitrobenzene, aniline, xylene, pyridine, moderately soluble in amyl alcohol, acetic acid or carbon tetrachloride and dyes wool in yellow shades from an acid bath. Concentrated sulphuric acid dissolves it forming violet blue solution. (Found: Cl, 9.54.  $C_{24}H_{13}N_2Cl$  requires Cl, 9.73 per cent).

*Acenaphtheno-3-bromoacenaphthazine* was prepared in the same way as the preceding compound from 3-bromoacenaphthenequinone (0.39 g.) and the diamine (0.276 g.) in 30 c.c. of boiling glacial acetic acid and similarly purified and crystallised in yellow plates. It does not melt below  $815^\circ$  and it possesses properties similar to those of the last compound. (Found: Br, 19.84.  $C_{24}H_{13}N_2Br$  requires Br, 19.55 per cent).

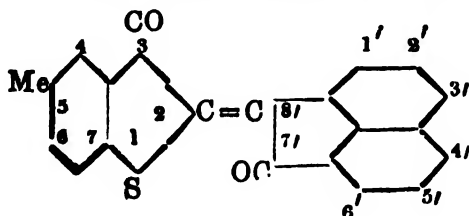
*Acenaphtheno-1-methoxyacenaphthazine*.—The brown solution, produced by boiling  $\beta$ -methoxyacenaphthenequinone (0.424 g.) and the diamine (0.368 g.) in 36 c.c. of glacial acetic acid for half an hour, was allowed to stand in the cold. The crystalline brownish-yellow precipitate, that separated after 1 hour was collected, purified first by boiling with alcohol and then by precipitation with water from the least quantity of boiling glacial acetic acid. The resultant flocculent precipitate on heating became granular. This was filtered, washed with hot water and crystallised from pyridine in beautiful hexagonal brownish-yellow plates, m. p.  $298^\circ$ . It is soluble in benzene, xylene, chloroform, acetic acid, pyridine and sparingly soluble in alcohol, acetone and ether. It dissolves in concentrated sulphuric acid with a violet blue colour and dyes wool in yellow shades. (Found: N, 8.1.  $C_{25}H_{16}ON_2$  requires N, 7.77 per cent).

*Acenaphtheno-3:4-dinitroacenaphthazine* separated gradually in shining chocolate coloured rectangular crystalline precipitate on heating for 1 hour the dark brown solution, produced by bringing together 3:4-dinitroacenaphthenequinone (0.272 g.) and 2:3-diaminoacenaphthene

(0.184 g.) in 75 c.c. of boiling glacial acetic acid. It was further purified by boiling successively with alcohol and acetic acid and finally crystallised from xylene in prisms; when strongly heated above  $315^{\circ}$  the azine sublimes. It is soluble in pyridine, xylene, aniline, sparingly soluble in alcohol, acetic acid, carbon tetrachloride and amyl alcohol. It gives a deep green solution in strong sulphuric acid and dyes wool in chocolate shades from an acid bath. (Found: N, 13.68.  $C_{24}H_{12}O_4N_4$  requires N, 13.33 per cent).

**1-Methoxyacenaphthaphenazine.**—The pale yellow solution produced by heating  $\beta$ -methoxyacenaphthenequinone (0.212 g.) and *o*-phenylenediamine (0.100 g.) in 52 c. c. of boiling glacial acetic acid for 20 minutes deposited no precipitate when cooled. The bulk of the solution was then reduced to 22 c. c. by the distillation of acetic acid and water added just to precipitate the product. It was redissolved by heating and allowed to cool. The separated needle shaped crystals were collected, washed with 50% acetic acid and hot water and finally recrystallised from dilute acetic acid in fine silky pale yellow needles, m. p.  $187-88^{\circ}$  (cf. Staudinger and others, *loc. cit.*). (Found: N, 9.65.  $C_{19}H_{12}ON_2$  requires N, 9.85 per cent).

**2-(5-Methyl)-thionaphthene-acenaphthyleneindigo.**



A solution of acenaphthenequinone (0.864 g.) in 50 c.c. of boiling glacial acetic acid was mixed with 5-methyl-3-hydroxythionaphthene (0.828 g.) dissolved in 30 c.c. of hot glacial acetic acid. The mixture turned reddish-brown. On adding strong hydrochloric acid (8 c.c.) and shaking for 2-3 minutes silky scarlet red needle shaped crystals separated. The whole of the mixture was heated to boiling for 10-12 minutes to complete the reaction, filtered hot, washed with acetic acid and hot water. For purification it was boiled successively with alcohol and glacial acetic acid and finally crystallised from xylene in fine needles, m. p.  $265-66^{\circ}$ . It is soluble in chloroform, amyl alcohol, benzene, xylene, nitrobenzene, aniline and pyridine, difficultly soluble in acetic acid, sparingly soluble in acetone, alcohol, ether, insoluble in ammonia and caustic alkalis. It dyes cotton in

scarlet red shade from an alkaline hydrosulphite vat and wool in the same colour from an acid bath. (Found: S, 9.56.  $C_{21}H_{12}O_2S$  requires S, 9.75 per cent).

2-(5-Methyl)-thionaphthene-8'(3'-chloro)acenaphthyleneindigo, similarly prepared from 3-chloroacenaphthenequinone (0.65 g.) and 5-methyl-3-hydroxythionaphthene (0.492 g.) in 63 c.c. of glacial acetic acid and 7 c.c. of concentrated hydrochloric acid, crystallised from pyridine in clusters of scarlet red rectangular crystals, m. p. 284-85° (with previous shrinking at 281°). It dyes wool in bright pleasant scarlet red shade from an acid bath and cotton in deep scarlet red shade from an alkaline hydrosulphite vat. All other properties resemble those of the preceding compound. (Found: Cl, 10.1.  $C_{21}H_{11}O_2ClS$  requires Cl, 9.8 per cent).

2-(5-Methyl)-thionaphthene-8'(3'-bromo)acenaphthyleneindigo, prepared in the same way as the two preceding compounds from 3-bromoacenaphthenequinone (0.52 g.) and the methylhydroxy-thionaphthene (0.328 g.) in 51 c.c. of glacial acetic acid and 5 c.c. of strong hydrochloric acid, separated from toluene in slender scarlet red rectangular crystals, m. p. 282°. It resembles the last compound in its properties. (Found: Br, 19.58.  $C_{21}H_{11}O_2BrS$  requires Br, 19.65 per cent).

2-(5-Methyl)-thionaphthene-8'(1'-methoxy)acenaphthyleneindigo.—The pinkish red solution, obtained by mixing  $\beta$ -methoxyacenaphthenequinone (0.424 g.) dissolved in 50 c.c. of boiling glacial acetic acid with methyl hydroxythionaphthene (0.328 g.) in 25 c.c. of hot acetic acid, was treated with concentrated hydrochloric acid (12 c.c.) and shaken thoroughly. The solution turned beautiful deep violet red and immediately deposited deep scarlet red needles. It was then heated to boiling for 30 minutes. The precipitate was collected and purified by heating it with alcohol and with moderately strong acetic acid and crystallised from acetic acid as deep scarlet red fine needles, m. p. 279-80°. It dyes wool in deep red shades from an acid bath and in pink colour on cotton from an alkaline hydrosulphite vat. The solubility of this dye resembles that of the preceding compounds in this series. (Found: S, 9.26.  $C_{22}H_{14}O_3S$  requires S, 8.98 per cent).

I take this opportunity of expressing my thanks to Dr. K. S. Caldwell, Principal, Science College, Patna, and to Dr. A. C. Sircar, M.A., Ph. D., for their kind encouragement in the work.

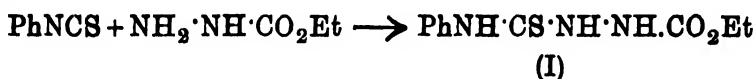


# Formation of Heterocyclic Compounds from some Derivatives of Ethyl Carbazinate.

By D. N. MAJUMDAR AND P. C. GUHA

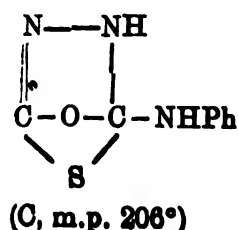
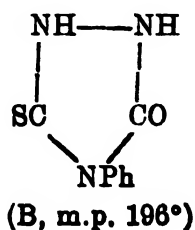
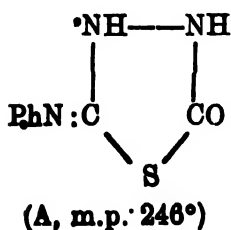
It has been shown by Guha and Guha (*J. Indian Chem. Soc.*, 1927, **4**, 161, 239) that dithiocarbazinic ester reacts with thiocarbimides, acid chlorides, diketones etc., to give rise to interesting heterocyclic compounds. The present investigation was undertaken with a view to making a comparative study of the behaviour of some typical derivatives of ethyl carbazinate and ethyl dithiocarbazinate towards the formation of heterocyclic compounds, from which idea can be formed as to the respective influence exerted by the oxygen and the sulphur atoms in the process of ring-closure.

Ethyl carbazinate reacts with mustard oils to yield carbethoxythiosemicarbazides identical with those obtained by Fromm (*Ber.*, 1923, **56**, 1370) from thiosemicarbazides by the action of chloroformic ester.

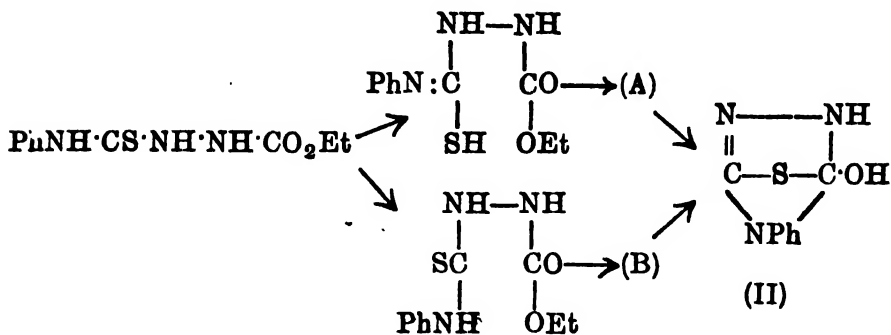


Carbethoxythiosemicarbazides do not lend themselves to ring-closure on being merely boiled with water or alcohol as has been observed by Guha and Guha (*loc. cit.*) in the case of the corresponding thiosemicarbazide dithiocarboxylates,  $\text{RNH} \cdot \text{CS} \cdot \text{NH} \cdot \text{CS} \cdot \text{SEt}$ .

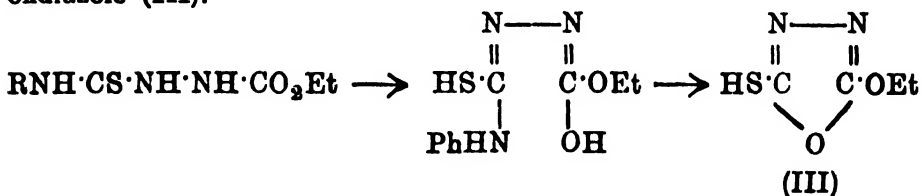
Compound (I) on treatment with 2 *N*-caustic potash yields by the elimination of a molecule of alcohol, a compound of the composition  $\text{C}_8\text{H}_7\text{ON}_3\text{S}$ . It melts at 283-84°. Though the compound is soluble in alkali, it cannot be desulphurised by treatment with red oxide of mercury showing the presence of the sulphur atom as a member of the ring (*cf.* Guha, *J. Amer. Chem. Soc.*, 1922, **44**, 1502). Three compounds, A (Guha and Sen, *J. Indian Chem. Soc.*, 1927, **4**, 44), B (Arndt, Milde, Tschenschner, *Ber.*, 1922, **55**, 341), C (Guha and Janniah, *J. Indian Inst. Sci.*, 1933, **16A**, 23) of this composition are already known and possess different melting points. There is,



however, another possible formula for the new compound viz., 4-*N*-phenyl-3-oxy-3:5-endothio-1:2:4-triazole (II) which can be formed from the carbethoxyphenylthiosemicarbazide through the transient intermediate stages A or B as follows:

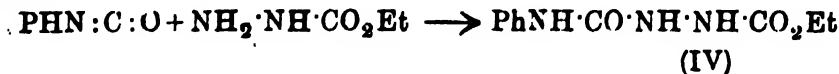


By the action of strong hydrochloric acid compound (I) loses a molecule of aniline and there is formed 3-ethoxy-5-thiol-4:1:2-oxdiazole (III).

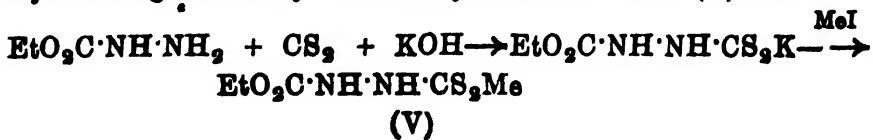


That the sulphur atom in compound (III) is not a member of the ring is proved by its desulphurisation with red oxide of mercury; as a mercaptan it also forms a disulphide.

Carbazinic ester reacts with phenyl isocyanate to yield 4-phenylsemicarbazide-1-carboxylate (IV) which does not lend itself to any sort of ring formation though from the corresponding dithiocarboxylate Guha and Guha (*loc. cit.*) obtained 2-phenylimino-3-acetyl-5-methylthiol-2:3-dihydro-4:1:2-oxdiazole by the action of acetic anhydride.

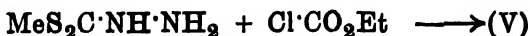


Ethyl carbazinate reacts with carbon disulphide and alcoholic potash to yield potassium carbethoxydithiocarbazinate which, with methyl iodide gives methyl carbethoxydithiocarbazinate (V) thus:

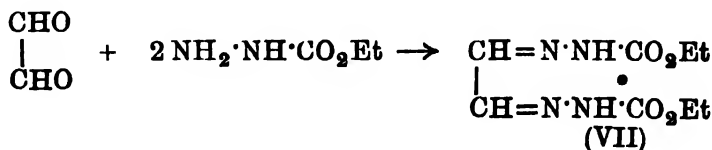
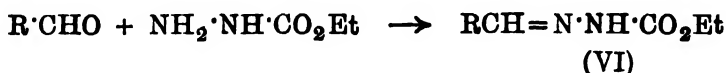




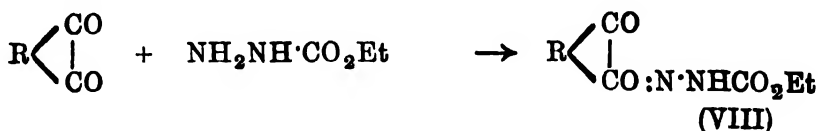
The correctness of the structure of compound (V) has been established by its synthesis from ethyl chlorocarbonate and methyl dithiocarbazinate.



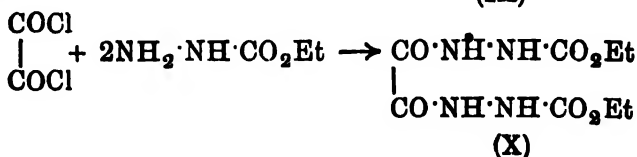
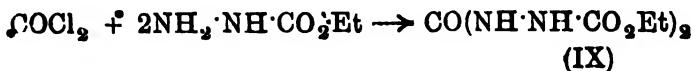
The action of mono- and dialdehydes on ethyl carbazinate proceeds in the normal way yielding the corresponding carbethoxy hydrazones ;



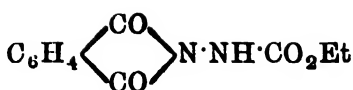
Guha and De (*J. Indian Chem. Soc.*, 1926, 2, 228) obtained closed ring thiocarbonylhydrazones from thiocarbonylhydrazide and *o*-diketones, similar participation of both of the keto groups of *o*-diketones in their reaction with methyl dithiocarbazinate to form oxadiazine rings has been observed by Guha and Guha (*loc. cit.*). Ethyl carbazinate reacts, however, with only one of the ketonic groups of the diketones to form the monocarbethoxyhydrazones (VIII)



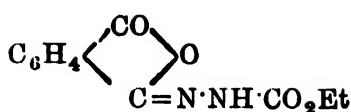
Carbonyl and oxalyl chlorides yield carbodicarbazinic ester (IX) and oxalyldicarbazinic ester (X) respectively, and not any ring compound as was the case with methyl dithiocarbazinate in its reaction with diacid chlorides (Guha and Guha, *loc. cit.*, p. 241).



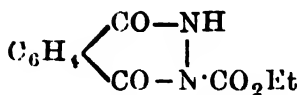
Phthalyl chloride reacts with carbazinic ester to yield a compound  $\text{C}_{11}\text{H}_{10}\text{O}_4\text{N}_2$  which though stable towards boiling water is decomposed into phthalic acid and carbazinic ester when heated with strong hydrochloric acid. Of the four possible formulæ (XIa, XIb,



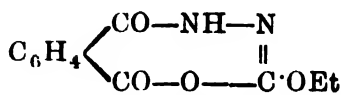
(XIa)



(XIb)



(XIc)



(XIId)

XIc, XIId), (XIc) and (XIId) necessitate the  $\alpha$ -iminohydrogen of the carbazinic esters to participate in ring formation which from a consideration of the general inertness observed in other reactions, does not seem to be very likely; besides a compound of formula (XIId) possessing an eight-membered ring with the grouping  $\text{CO} \cdot \text{O} \cdot \text{CO}$  present in it cannot be expected to be stable.

#### EXPERIMENTAL.

*Ethyl carbazinate* was prepared according to the method of Theile and Lachmann (*Annalen*, 1895, 288, 267) modified as follows: The benzaldehyde compound of the crude carbazinic ester was hydrolysed with concentrated hydrochloric acid by heating carefully and the resulting solution extracted with hot benzene. The acid solution was evaporated on a water-bath almost to dryness and the separated light yellow needles of the hydrochloride dried in vacuum over soda lime and concentrated sulphuric acid.

*Ethyl 4-phenylthiosemicarbazide-1-carboxylate* (I).—Ethyl carbazinate hydrochloride (5.2 g.) dissolved in alcohol (50 c.c.) was slowly added to a mixture of phenylmustard oil (5 g.) and anhydrous sodium carbonate (3.9 g.) dissolved in minimum quantity of water and the mixture heated under reflux during 3 hours on a water-bath. The alcoholic solution was filtered off from the precipitated sodium chloride and the filtrate concentrated to a small bulk. On cooling a quantity of oily substance settled at the bottom which soon solidified. This after being freed from unreacted carbazinic ester crystallised from alcohol in needles, m.p. 141.42°. It is soluble in dilute alkali. (Found: N, 17.51.  $\text{C}_{10}\text{H}_{13}\text{O}_3\text{N}_2\text{S}$  requires N, 17.57 per cent).

*4-Phenylimino-3-hydroxy-3:5-endothio-2:3-dihydro-1:3:4-triazole* (II).—Carbethoxyphenylthiosemicarbazide (2 g.) dissolved in excess of 2N-KOH solution was heated under reflux on a sand-bath during 4 hours. The solution after acidification with dilute hydrochloric acid

was concentrated to a small volume and potassium chloride precipitated by alcohol filtered off. The filtrate on concentration and cooling gave a solid which crystallised from alcohol in fine white needles, m.p. 283-84° (decomp.) It is soluble in dilute alkali and remained unchanged on mercuric oxide treatment. (Found: N, 21.15.  $C_8H_7ON_3S$  requires N, 21.24 per cent).

3-Ethoxy-5-thiol-4:1:2-oxdiazole (III).—Carbethoxysphenylthiosemicarbazide (2 g.) was boiled under reflux with concentrated hydrochloric acid (50 c.c.) for 2 hours. The excess of acid was nearly neutralised with dilute sodium hydroxide and the solution concentrated to a smaller bulk and the sodium chloride precipitated by alcohol filtered off. The filtrate was evaporated to dryness and the residue crystallised from alcohol in fine microscopic needles, m.p. 274-75° (decomp.). It is soluble in alkali, yields a disulphide with iodine and can easily be desulphurised by red oxide of mercury. (Found: N, 19.01.  $C_4H_6O_2N_2S$  requires N, 19.1 per cent).

4-Phenylsemicarbazide-1-carboxylate (IV).—To ethyl carbazinate generated from the hydrochloride (2.4 g.) was added phenylisocyanate (2 g.) gradually with constant shaking and the mixture heated under reflux for 15 minutes on a water-bath and filtered hot. The filtrate on dilution with water gave a brownish oil which soon solidified. It was then powdered and shaken repeatedly with ether to remove diphenylcarbamide formed by the action of water on the isocyanate. The ether insoluble residue after being washed with dilute hydrochloric acid and water was crystallised from alcohol in prisms, m.p. 154-55°. It is insoluble in alkali. (Found: N, 19.84.  $C_{10}H_{11}O_2N_3$  requires N, 20.48 per cent).

Methyl carbethoxydithiocarbazinate (V).—Ethyl carbazinate hydrochloride (2.8 g.) and carbon disulphide (1.5 g.) were taken in a flask together with alcohol sufficient to dissolve the hydrochloride. To this an alcoholic solution of potassium hydroxide (1.1 g.) was added gradually under shaking and the mixture gently warmed on a water-bath. After cooling, methyl iodide (4.0 g.) was added and the reaction mixture after standing for  $\frac{1}{2}$  hour was poured into water and extracted with ether, the extract shaken several times with dilute hydrochloric acid and then with water. After removal of ether, the residue was crystallised from alcohol in colourless needles, m.p. 90-91°. (Found: N, 14.35.  $C_5H_{10}O_2N_2S_2$  requires N, 14.4 per cent).

Compound (V) was also prepared by the action of chlorocarbonic ester on methyl dithiocarbazinate prepared according to the method

of Busch (*J. pr. Chem.*, 1916, 93, 59). It had m.p. 90-91° which remained undepressed on admixture with a sample prepared by the foregoing method.

*Ethyl o-nitrobenzylidencarbazinate* (VI,  $R = o\text{-C}_6\text{H}_4\cdot\text{NO}_2$ ).—To an alcoholic solution of *o*-nitrobenzaldehyde (2.8 g.) and ethyl carbazinate hydrochloride (3 g.) was added an aqueous solution of anhydrous sodium carbonate (3.25 g.) and the mixture heated under reflux for  $\frac{1}{2}$  hour on a water-bath. The solution was filtered off from the precipitated sodium chloride and the filtrate on concentration and cooling gave a crystalline solid which after being washed with dilute acid and water was recrystallised in light yellow needles from alcohol, m.p. 130-31°. (Found: N, 18.4.  $\text{C}_{10}\text{H}_{12}\text{O}_4\text{N}_3$  requires N, 18.65 per cent).

*Ethyl salicylidencarbazinate* (VI,  $R = \text{C}_6\text{H}_4\text{OH}$ ) crystallised from alcohol in plates, m.p. 129-30°. (Found: N, 13.39.  $\text{C}_{10}\text{H}_{12}\text{O}_3\text{N}_2$  requires N, 13.46 per cent).

*Ethyl p-tolylidencarbazinate* [VI,  $R = \text{C}_6\text{H}_4\text{CH}_3$ , (*p*)] crystallised from alcohol in light yellow needles, m.p. 116-18°. (Found: N, 18.42.  $\text{C}_{11}\text{H}_{14}\text{O}_2\text{N}_2$  requires N, 13.39 per cent).

*Ethyl cinnamylidencarbazinate* (VI,  $R = \text{C}_6\text{H}_5\text{CH}:\text{CH}$ ) crystallised from alcohol in colourless needles, m.p. 196-97°. (Found: N, 12.78.  $\text{C}_{12}\text{H}_{14}\text{O}_2\text{N}_2$  requires N, 12.84 per cent).

*Ethyl piperonylidencarbazinate* (VI,  $R = \text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3$ ) crystallised from alcohol in colourless needles, m.p. 123-24.5°. (Found: N, 12.0.  $\text{C}_{11}\text{H}_{12}\text{O}_4\text{N}_2$  requires N, 11.87 per cent).

*Ethyl furfurylidencarbazinate* (VI,  $R = \text{C}_4\text{H}_3\text{O}$ ) crystallised from alcohol in light brown needles, m.p. 132.5-33.5°. (Found: N, 15.29.  $\text{C}_8\text{H}_{10}\text{O}_3\text{N}_2$  requires N, 15.38 per cent).

*Ethyl vanilinidencarbazinate* [VI,  $R = \text{C}_6\text{H}_3(\text{OCH}_3)\text{OH}$  (3:1)] crystallised from alcohol in light brown needles, m.p. 152.5-53.6°. (Found: N, 11.69.  $\text{C}_{11}\text{H}_{14}\text{O}_4\text{N}_2$  requires N, 11.77 per cent).

*Ethyl glyoxylidenedicarbazinate* (VII).—Ethyl carbazinate hydrochloride (2 g.) and sodium glyoxal bisulphite (1.82 g.) were dissolved in water and heated on a water-bath for 1 hour, when a white precipitate separated which being insoluble in ordinary organic solvents could not be crystallised. It was boiled with alcohol and dried at 100°, m.p. 305-06° (decomp.). (Found: N, 28.58.  $\text{C}_8\text{H}_{14}\text{O}_4\text{N}_4$  requires N, 28.60 per cent).

*Camphorquinone monocarbethoxyhydrazone* (VIII).—To an alcoholic solution of camphorquinone (1.18 g.) and ethyl carbazinate

hydrochloride (1 g.) was added an aqueous solution of anhydrous sodium carbonate (0.75 g.) and the mixture heated under reflux for 8 hours on a water-bath. The filtered solution was concentrated almost to dryness and the sodium chloride removed after precipitation with absolute alcohol. The filtrate on concentration and cooling gave a crystalline solid which after being washed with ether was recrystallised from alcohol in colourless needles, m.p. 199.5-200°. (Found: C, 62.1; H, 8.84; N, 11.02.  $C_{13}H_{20}O_3N_2$  requires C, 61.9; H, 7.93; N, 11.19 per cent).

*Phcanthraquinone monocarbethoxyhydrazone*.—An aqueous alcoholic solution of phenanthraquinone (2.9 g.), ethyl carbazinate hydrochloride (2.0 g.) and anhydrous sodium carbonate (1.5 g.) was heated under reflux for 8 hours on a water-bath and the separated solid after being shaken with hot benzene, was washed with dilute acid and then with water. It is insoluble in all the ordinary organic solvents and could only be obtained as a brown amorphous powder from pyridine, m.p. above 320° after softening at 275°. (Found: N, 9.8.  $C_{17}H_{14}O_3N_2$  requires N, 9.53 per cent).

*Acetophenone carbethoxyhydrazone* [ $C(PhMe)=N \cdot NH \cdot CO_2Et$ ].—It was prepared by a process similar to that adopted from the preparation of the foregoing compound and was crystallised from alcohol in fine colourless needles, m.p. 119.6-20.6°. (Found: N, 13.41.  $C_{11}H_{14}O_2N_2$  requires N, 13.59 per cent).

*Carbodicarbazinic ester* (IX).—A mixture of carbonyl chloride (5 c.c. of 20% solution in toluene), ethyl carbazinate hydrochloride (2.0 g.) and anhydrous sodium carbonate (0.8 g.) in dry benzene (20 c.c.) was heated under reflux for 3 hours on a water-bath. The contents of the flask were filtered and the filtrate evaporated to dryness, the residue crystallised from alcohol in colourless needles, m.p. 119-20°. (Found: N, 23.75.  $C_7H_{14}O_5N_4$  requires N, 23.9 per cent).

*Oxalyldicarbazinic ester* (X).—The compound was obtained by the above process using oxalyl chloride and was crystallised from alcohol in colourless plates, m.p. 182-83° (decomp.). (Found: N, 21.08.  $C_8H_{14}O_6N_4$  requires N, 21.37 per cent).

*o-Phthalalydicarbazinic ester* (XI).—A mixture of phthalyl chloride (2.9 g.), ethyl carbazinate hydrochloride (2.0 g.) and anhydrous sodium carbonate (2.5 g.) in dry benzene was heated under reflux for about 1 hour on a water-bath. The contents of the flask were filtered off from the separated sodium chloride and the filtrate

evaporated to dryness. The residue was shaken with a solution of sodium bicarbonate to remove phthalic acid formed during the reaction and some unreacted phthalyl chloride washed with dilute acid and water and crystallised from alcohol in fine colourless needles, m.p. 166-67°. It is soluble in cold alkali and is decomposed by boiling concentrated hydrochloric acid into ethyl carbazinate and phthalic acid. (Found: N, 12.25.  $C_{11}H_{10}O_4N_2$  requires N, 12.0 per cent).

*Action of ethyl chlorocarbonate upon ethyl carbazinate: formation of ethyl hydrazinedicarboxylic ester.*—To a mixture of an alcoholic solution of ethyl carbazinate hydrochloride (2.0 g.) and an aqueous solution of sodium carbonate (0.8 g.), chlorocarbonic ester (2 g.) was gradually added with constant stirring. The mixture was warmed on a water-bath for about an hour and the separated sodium chloride filtered off. The filtrate gave on concentration and cooling a solid which crystallised from alcohol in needles, m.p. 131.5-32.5°. (Found: N, 15.8.  $C_6H_{12}O_4N_2$  requires N, 15.9 per cent).

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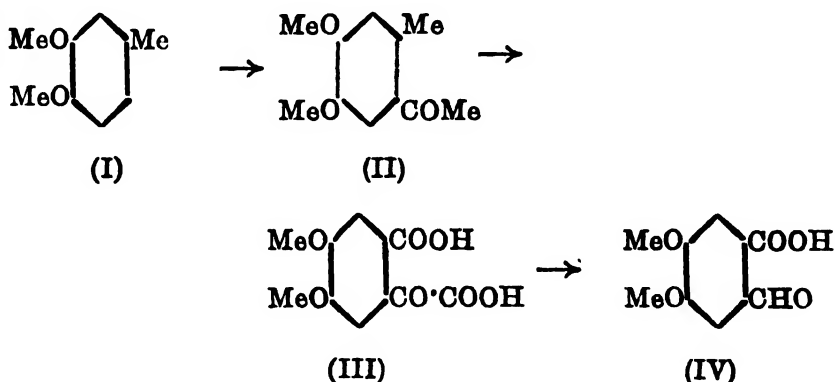
Received September 11, 1933.

A note of correction.—The compound described in this journal (1928, 5, 163) as 2-phenylhydrazino-1:3:4-thiodiazole was prepared in this laboratory in connection with some other work and was found to contain N, 26.34 and S, 15.20 (not 16.92 as reported before) agreeing with the composition  $C_8H_{10}ON_4S$  which fits in well with the formula of formylphenylthiocarbohydrazide,  $PhNH \cdot NH \cdot CS \cdot NH \cdot NH \cdot CHO$ .

# A New General Method for Synthesis of *o*-Aldehydo-carboxylic Acids. A Preliminary Note.

BY SATYENDRA NATH CHAKRAVARTI.

There are very few really good methods available for the synthesis of substituted *o*-aldehydo acids. Thus the majority of the monomethoxy- and dimethoxy-*o*-aldehydo acids have either still to be synthesised or have been synthesised by methods which are either not of general application or are too tedious. At the time when these researches were started, only *m*-opianic acid and opianic acid had been synthesised. The synthesis of *m*-opianic acid was first accomplished by Perkin and Fargher (*J. Chem. Soc.*, 1921, 119, 1724) in accordance with the scheme:—



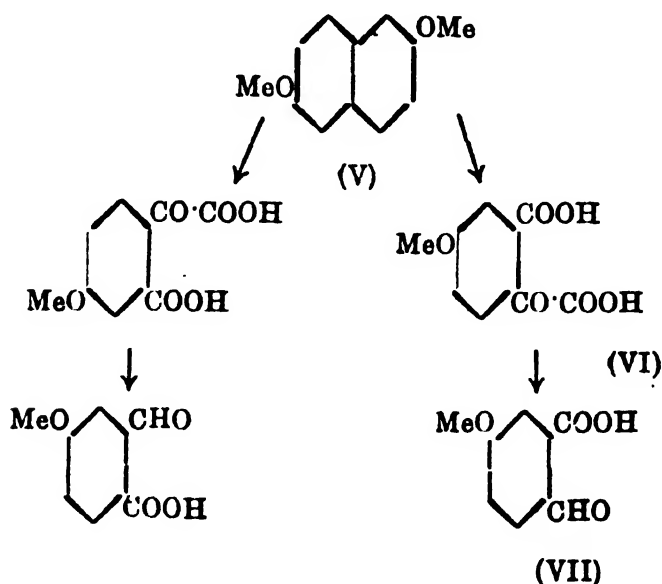
Unfortunately this excellent synthesis cannot be generally applied, firstly because it is very difficult to introduce the acetyl group in the required position and secondly, because the oxidation of substances of the type (II) give rise to a variety of different products which are often difficult to separate. Reimer-Tiemann's reaction cannot also be used as a general method for the synthesis of *o*-aldehydo acids (*cf.* Perkin and Stoye, *J. Chem. Soc.*, 1928, 123, 3172).

The only other method which has been tried successfully is the method of the oxidation of phthalides. Thus opianic acid has been obtained by the oxidation of meconine.

This method is, also, of only limited application as is shown by the failure of attempts of direct oxidation of  $\psi$ -meconine (Solomon, *Ber.*, 1887, 20, 688; Edward, Perkin and Stoye, *J. Chem. Soc.*, 1925, 196; Chakravarti, *J. Indian Chem. Soc.*, 1929, 6, 208), of 8:4.

methoxylenedioxyphthalide (Perkin and Trikofus, *J. Chem. Soc.*, 1926, 2931), of 4:5-methylenedioxyphthalide (Stevens and Robertson, *ibid.*, 1927, 2791) and of 4-methoxyphthalide (Chakravarti and Perkin *ibid.*, 1929, 197). The present author tried a number of devices to to get over this difficulty (*loc. cit.*, p. 209). In the case of  $\psi$ -meconine, more recently still, Robinson and Greenwood succeeded in converting it into  $\psi$ -opianic acid by first converting  $\psi$ -meconine into  $\beta$ - $\psi$ -gnos-copine and then oxidising it (*J. Chem. Soc.*, 1932, 1371)

The present author tried to devise a number of general methods for synthesising methoxy-*o*-aldehydo acids in 1928. As a result of this and subsequent work, two general methods have been developed, one starting from the hydrindones, and the other from the substituted derivatives of naphthalene. In the latter method, symmetrically disubstituted or symmetrically tetrasubstituted naphthalene derivatives are oxidised with alkaline permanganate under special conditions. To take an example, when 2:6-dimethoxynaphthalene (V) is oxidised, 5-methoxyphthalonic acid (VI) is first formed which is readily converted into 5-methoxyphthalaldehydic acid (VII)



The idea behind the synthesis is that whichever benzene ring is ruptured during oxidation, a methoxyphthalonic acid must be formed under suitable conditions. A number of such synthesis has been effected and an account of the synthesis of all the methoxyphthalaldehydic acids and the three opianic acids by this method is reserved for a future communication.



## EXPERIMENTAL.

As a result of a series of comparative experiments, the following two conditions of oxidation were arrived at as giving the best yields of the substituted phthalaldehydic acids.

(i) A mixture of the substituted naphthalene ( $\frac{1}{2}$  mol.), sodium hydroxide (1 mol.), 6% aqueous potassium permanganate solution (8 mol.) were heated together with constant shaking till decolorised (3 to 4 hours). The oxidation was generally effected in 20 g-wts.

(ii) In a 2 litre flask provided with a good mechanical stirrer, a reflux apparatus and a dropping funnel, the substituted naphthalene derivative (0.25 mol.) was suspended in 2% solution of sodium hydroxide (250 c.c.) and the mixture heated to boiling. To the boiling solution was added gradually during the course of 2 hours a hot 10% aqueous potassium permanganate solution ( $2\frac{3}{8}$  mols). After the last addition of permanganate, the mixture was boiled for another  $\frac{1}{2}$  hour to complete the oxidation.

The oxidation product was generally worked up as described below in the case of 2:6-dimethoxynaphthalene. Yields of the final o-aldehydo acids vary from 15 to 40%. Oxidations under condition (i) generally give larger quantities of the phthalic acids, although the net yield of the substituted o-aldehydo acids is as good, if not better as under the condition (ii). Under condition (ii), more of the starting substance is left unoxidised. For obtaining the best yields it is necessary to have the naphthalene derivative in as pure a state as possible.

During these experiments it has been found that if the object is to synthesise the aldehydo acids, it is not at all necessary to isolate the substituted phthalonic acids, as the aldehydo acids crystallise much better. •

*Preparation of 2:6-dimethoxynaphthalene.*—2:6-Dihydroxynaphthalene was prepared and purified according to the directions given by Willstätter and Parans (*Ber.*, 1907 40, 1410). Pure 2:6-dihydroxynaphthalene was converted into 2:6-dimethoxynaphthalene in almost quantitative yields by carrying out the methylation with dimethylsulphate in methyl alcohol solution, sodium hydroxide solution being added gradually from time to time so as to keep the solution just alkaline.

*Oxidation of 2:6-dimethoxynaphthalene* was carried out as described under (i) and (ii). After the oxidation was over, the mixture

was cooled and the precipitated manganese dioxide and the unchanged substance were filtered off. The filtrate was made just acid with concentrated hydrochloric acid and then evaporated to dryness. The residue was then dissolved in water, the solution neutralised and treated with excess of sodium bisulphite (generally for 1 mol. of the naphthalene, 2 mol. of the bisulphite were used) and evaporated to dryness on the steam-bath and then the residue heated for  $\frac{1}{2}$  hour at  $120^{\circ}$  in an air oven. The residue thus obtained was then twice stirred up with excess of concentrated hydrochloric acid and evaporated to dryness on the steam-bath in an open dish. This residue was then extracted twice with boiling benzene and the combined benzene extract allowed to remain for a few hours when small amount of substance (A) rapidly separated. The filtrate from this was concentrated to a small volume and allowed to crystallise. A crystalline substance soon separates, the melting point of which in crude state is  $125^{\circ}$ . On repeated crystallisation from water, the substance separated in beautiful rosettes of needles, m.p.  $144^{\circ}$ . This substance is 5-methoxyphthalaldehydic acid. (Found: C, 59.9, 59.8; H, 4.4, 4.3.  $C_9H_8O_4$  requires C, 60.0; H, 4.4 per cent). The identity of this substance was established by taking the mixed melting point with 5-methoxyphthalaldehydic acid obtained from 5-methoxyphthalonic acid. It also forms an oxime.

The substance (A) was found to be very sparingly soluble in benzene and very readily so in cold water. On reboiling with benzene it melts at about  $150^{\circ}$  and is probably impure 4-methoxyphthalic acid. It is also likely that the mother liquors from 5-methoxyphthalaldehydic acid may contain small amounts of 4-methoxyphthalaldehydic acid. This point is being further investigated.

In a preliminary experiment attempts were made to isolate the phthalonic acid first. But this acid does not crystallise readily and is difficult to isolate in view of the fact that it is far more soluble in water than in benzene. An aqueous solution of the phthalonic acid obtained from 2:6-dimethoxynaphthalene was treated with an acetic acid solution of phenylhydrazine when on vigorous stirring and allowing to remain a pale yellow crystalline substance separated, m.p.  $200^{\circ}$ . On repeated recrystallisations yellow coloured needles, m.p.  $223^{\circ}$  were obtained. This substance was found to be identical with 6-methoxy-3-phenyl-phthalozon (4) carboxylic acid (1) obtained from 5-phthalonic acid by the method of mixed melting points.

*Synthesis of 5-methoxyphthalaldehydic acid* was effected according to the conditions described before (Chakravarti and Perkin, *loc. cit.*, p. 199). It was then oxidised to 5-methoxyphthalonic acid by the method of Fritsch (*Annalen*, 1897, 296, 359). 5-Methoxyphthalonic acid (11.5 g.) was dissolved in sodium carbonate solution (5.6 g. in 55 c.c.), and the solution evaporated to dryness. The residue was dissolved in 10% sodium bisulphite solution (40-50 c.c.) and evaporated to dryness on the water-bath. This residue was heated for an hour at 120° and then treated twice with concentrated hydrochloric acid and the solution evaporated to dryness. The residue was completely extracted with benzene. On concentrating the benzene solution and allowing to stand, a crystalline substance was deposited. On being recrystallised twice from water 5-methoxyphthalaldehydic acid separated in beautiful needles, m.p. 144°. (Found: C, 59.9; H, 4.3.  $C_9H_8O_4$  requires C, 60.0; H, 4.4 per cent).

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## **Influence of Light on Nitrification in Soil.**

By N. R. DHAR, A. K. BHATTACHARYA AND N. N. BISWAS.

In previous publications from these laboratories (Gopala Rao and Dhar, *Soil Sci.*, 1931, **31**, 379 ; Dhar and Gopala Rao, *Sir P. C. Ray Comm. Vol., J. Indian Chem. Soc.*, 1933, 81 ; Dhar, Bhattacharya and Biswas, *Soil Sci.*, 1933, **35**, 281), it has been shown that nitrification in soils of tropical countries is more photochemical in nature than bacterial.

The object of this paper is (i) to show from exactly comparable experiments that the amounts of ammonium salts oxidised are much greater in presence of sunlight than in the dark with both sterilized and unsterilized soil ; the conditions for the experiments on nitrification were more or less similar to those occurring under natural conditions in the field; (ii) to show that more ammonia and nitrite are formed from urea and egg yellow in some in sunlight than in the dark; (iii) to show that the phenomenon of ammonification in soil is mainly an oxidation reaction accelerated by light, in case of temperature and aeration and soil surface and; (iv) to show briefly that the existing theories, explaining the increased production of ammonia and nitrate on drying the soil, on heating it or baking it in sunlight or sterilizing it by volatile antiseptics, are insufficient and to suggest a new explanation of the observations.

### **EXPERIMENTAL.**

A hole was dug 9" deep in the grass land in the laboratory compound for the collection of the soil, which was not manured for some years. The soil was crushed, passed through a sieve with 1 mm. bore and dried in air at 80°. For sterilizing the soil, it was heated in an air-oven for 180 hours at 140°. All the chemicals and glass apparatus used in the experiments were sterilized in an autoclave at 20 lbs. pressure for an hour. The distilled water was sterilized by boiling.

For the nitrification experiments, 500 g. of the soil were mixed, with 5 g. of ammonium salts and 189 g. of sterilized distilled water exposed to light in loosely covered glass vessels or

about a year beginning from 2nd August 1932. During this period, on three occasions (10th August, 22nd October 1932 and 11th May 1933), 180 g. of sterilized distilled water were added and the soil containing the salts were carefully mixed up by stirring with sterile glass rod. Blank experiments under identical conditions were carried on in the dark by covering the glass vessels with a thick layer of black Japan enamel. For the experiments in the dark, these vessels were also placed in the sun to attain approximately the same temperature as those receiving sunlight.

After the completion of the exposure, the hard and dry soil was carefully powdered and 50 g. were taken out for analysis. The unchanged ammonium salt was estimated by adding potassium hydroxide in excess to the soil and distilling the ammonia set free and absorbing it with a standard solution of sulphuric acid. After the distillation of the ammonia, 1 g. of chemically pure Devarda's alloy was added to the soil containing alkali and the nitric nitrogen found by the oxidation of the ammonium salt was reduced to ammonia, which was distilled off and absorbed in sulphuric acid. In our experiments in order to drive off the first lot of ammonia, the flask containing the soil and ammonium salt and alkali was heated on a water-bath for more than 1 hour and then air was aspirated for  $\frac{1}{2}$  hour. The reduction of the nitric nitrogen by Devarda's alloy was carried on for 1 hour and again air was aspirated for  $\frac{1}{2}$  hour. We have tested in our experiments that heating with caustic alkali for a longer period does not appreciably increase the amount of ammonia liberated.

For the experiments on ammonification with egg-yellow, fresh eggs were carefully washed with dilute solutions of potassium permanganate and broken with a sterile glass rod and the yellow was separated from the egg-white and a suspension was prepared in a sterile flask with sterilized distilled water. The suspension was mixed with different amounts of sterilized or unsterilized soil (or zinc oxide or titanium oxide) and exposed to light in 100 c.c. graduated cylinders. Another set was kept in the dark for comparison. Similar experiments were carried on with urea, which had already been sterilized by heating the solid in an autoclave. The loss of water due to evaporation was made up by the addition of sterile distilled water. These experiments were continued from November 1932 to March 1933. After the necessary exposure, the total nitrogen was estimated according to the method developed by Iodlbauer and Dyer

(cf. Thorpe and Whiteley "Organic chemical analysis", 1926, p. 82). The ammonia formed from ammonification was estimated by Folin's method. The total amount of nitrogen in the egg-yellow suspension was determined by the Kjeldahl method before the exposure was started.

The soil with which all the experiments were carried on was analysed for its ammonia and nitric nitrogen contents in exactly the same way as described in the nitrification experiments. The amounts of  $\text{NH}_3$  and  $\text{NO}_3$  in 100 g. of soil are 0.006 g. and 0.0078 g. respectively.

The experimental results are given in Table I.

TABLE I.

Nitrification of ammonium salts exposed to sunlight for 550 hours.

Condition.	Nature of soil.	Amount of salt unoxidised.	Amount of salt oxidised.	Percentage oxidised.
		$\text{NH}_4\text{Cl}$		
Sunlight	unsterilized	1.9 g.	2.6 g.	58
Dark	"	4.2	0.7	14
Sunlight	sterilized	2.3	2.8	50
Dark	"	4.4	0.5	10.2
		$(\text{NH}_4)_2\text{HPO}_4$		
Sunlight	unsterilized	1.85 g.	2.8 g.	60.2
Dark	"	4.4	0.55	11.1
Sunlight	sterilized	2.15	2.75	56
Dark	"	4.6	0.3	6.5
		$(\text{NH}_4)_2\text{HPO}_4$		
Sunlight	unsterilized	3.35 g.	1.15 g.	23
Dark	"	4.75	0.15	3
Sunlight	unsterilized	4.2	0.8	16
Dark	"	4.85	0.1	2

In obtaining these values, corrections due to the presence of very small amounts of ammonia and nitrate present in the original soil have been introduced.

20 G. of the original soil when shaken with 20 c.c. of water gave a  $p_H$  value 7.3. The  $p_H$  of the exposed soils varied from 6.6 to 7.1. It was observed that the  $p_H$  of the soils receiving sunlight was slightly less than those in the dark. This was due to the fact that in the vessels receiving the solar radiations, there was greater oxidation of the ammonium salts and the consequent replacement of the basic radical by an acidic substance.

From the foregoing results it will be seen that the total amounts of the ammonium salts did not materially differ after a year from the amounts introduced. In presence of light, the amounts varied from 4.5 to 5 g.; in the dark the variation was much less and it was from 4.9 to 5 g. which was the amount introduced. Hence in our experiments specially in the dark, there was practically no loss due to denitrification. As the estimations of ammonia and nitric nitrogen in the original soil, in the soil kept in the dark and in the soil exposed to sunlight were carried on exactly in the same manner, the results obtained are certainly comparative.

TABLE II.

Ammonification and nitrification of 2 per cent urea solutions exposed to sunlight for 225 hours.

	Wt. of soil in g.	Percentage of ammonia formed.	Percentage of nitrite formed.		Wt. of soil in g.	Percentage of ammonia formed.	Percentage of nitrite formed.
Unsterilized	1 (light)	15.7	10.8	Sterilized	20 (light)	14.54	10.8
	1 (dark)	8	6.5		20 (dark)	8.7	4.58
Sterilized	1 (light)	14	9.4	Unsterilized	50 (light)	19.58	12.7
	1 (dark)	6.52	5.76		50 (dark)	12.7	
Unsterilized	20 (light)	18.0	12.6	Sterilized	50 (light)	18.5	17.96
	20 (dark)	12.1	10.1		50 (dark)	8.9	7.97



TABLE III.

Ammonification and nitrification of 2 per cent suspensions of egg-yellow exposed to sunlight for 225 hours.

Wt. of soil or catalyst in g.	Percentage of ammonia formed.	Percentage of nitrite formed.	Wt. of soil or catalyst in g.	Percentage of ammonia formed.	Percentage of nitrite formed.
unsterilized { 1 (light)	17.8	4.02	unsterilized { 50 (light)	32.23	7.64
1 (dark)	7.88	2.46	50 (dark)	26.7	6.23
sterilized { 1 (light)	16.5	3.25	sterilized { 50 (light)	27.85	8.33
1 (dark)	9.45		50 (dark)	21.67	4.8
unsterilized { 20 (light)	24.3	6.95	unsterilized { 1 TiO <sub>2</sub> (light)	4.93	...
20 (dark)	16.5	2.46	1 TiO <sub>2</sub> (dark)	3.31	...
sterilized { 20 (light)	7.6	1.66	sterilized { 1 ZnO(light)	6.38	1.66
20 (dark)			1 ZnO(dark)	4.93	0

### DISCUSSION.

These experiments were carried on in tall glass cylinders and hence the amount of air available was small and the percentage of ammonification and nitrification has not been large but the experimental results show that in presence of light, the amounts of ammonia and nitrate formed are always greater than those in the dark with both the sterilized and unsterilized soil. Moreover, the amounts of ammonia formed are always greater than the amounts of nitrite obtained. It is also apparent from the foregoing experiments that the amounts of ammonia and nitrite formed increase with the amounts of the soil. This happens because both ammonification and nitrification are increased by an increase of the surface on which oxidation can take place.

The experimental results in Table I show that on exposing the ammonium salts to light mixed with soil, the greater part of the ammonium compound is oxidised to nitrite after 550 hours' exposure

to sunlight with ammonium phosphate and chloride. The sulphate is much less oxidised. The oxidation in the vessels coated with black japan enamel is much smaller than in those receiving light. If nitrification were mainly a bacterial process, the amount of nitrification in the vessels in the dark with unsterilized soil should not have been materially different from those exposed to light.

Moreover, the amount of nitrite formed in the vessels with the sterilized soil is not very different from the vessels containing the unsterilized soil, the maximum difference in the percentage nitrified in the sterilized and unsterilized soils does not exceed 8 per cent. The germicidal property of sunlight seems to be well known. According to Warington (*Chem. News*, 1877, **36**, 263), light hinders the activity of nitrifying organisms. Waksman ("Microbiology", 1927, p. 35) has stated that due to the antiseptic properties of solar radiations, the number of bacteria is less on the surface of soils exposed to sunlight. We are determining the number of nitrifying bacteria in our samples of soil and from our preliminary results obtained according to the silicic acid gel method of Winogradsky, we find that the number of nitrifying bacteria in a gram of the original soil is not far from 8000. When the soil is exposed to sunlight, the bacteria are likely to be killed due to the joint action of light and increased temperature and that is why the amount of nitrification in the vessels exposed to light and containing unsterilized soil is not markedly different from those containing the sterilized soil. Moreover, the nitrification in the vessels kept in the dark and containing unsterilized soil is not widely different from those with the sterile soil. It seems likely that due to the high temperature also prevailing in the dark vessels, the bacteria could not survive.

As the light and dark experiments are exactly comparable, any bacterial contamination due to the introduction of air containing dust particles would affect the nitrification in all sets equally because the experiments were conducted at the same place. The results of our experiments, however, show that nitrification is only prominent in vessels receiving sunlight and this is not likely to be a matter of chance only. A similar behaviour is observed in the ammonification experiments.

Last summer we measured the soil temperature at Allahabad and in the month of April, it went up to 50° at two inches deep. May and June, 1933, were frequently cloudy and the summer was a mild one. In the months of May, June and July, 1932, after exposing

ammonium salt solutions mixed with soil to sunlight for 700 hours, we get oxidation of 80% with ammonium chloride and 89% with ammonium phosphate, whilst in the dark, the figures were 4.8% for ammonium chloride and 1.4% for ammonium phosphate (*cf.* Dhar, Bhattacharyya and Biswas, *loc. cit.*). The summer of 1932 at Allahabad was more severe than that of 1933 and that is why there was greater oxidation of ammonium salts in light in 1932 than in 1933. Moreover, there is another factor; in the experiments carried on in the months of May, June and July, 1932, this ammonium salts and soil were always kept wet by the frequent addition of water, whilst for the experiment recorded in this paper, the soil was allowed to dry up completely in order to have the experimental conditions similar to those occurring under natural conditions in the field. The oxidation of ammonium salts is greater in the wet condition of the soil than when it is hard and dry. Leather, working at Pusa, stated that the maximum temperature at Pusa may rise to 70° at the soil surface and 60° at the depth of 1 or 2 inches.

In Egypt the recorded temperature is 65° at the surface and 56° at a depth of 2 inches. From recent measurements in our laboratory on the influence of temperature on bacterial nitrification, we find that 35° is the optimum temperature for bacterial nitrification, which becomes practically negligible at 50° due to the harmful influence of high temperature on bacteria. Hence in tropics, nitrification in soil cannot be much of bacterial origin in the months of April, May, June and July. In these very months, the amount of nitrate in soils is, however, the greatest (Compare Dhar and Gopala Rao, *loc. cit.*). Even in colder countries like England, Germany, etc., the soil temperature may go up to 35° or more in summer (*Vidg. Russel*, "Soil Conditions and Plant Growth", 1932, p. 468), although the optimum temperature for bacterial nitrification is stated to be 25° in cold countries. In these countries, bacterial nitrification must be greatly hindered in the summer months due to the soil temperature becoming much greater than the optimum temperature for bacterial nitrification, though the nitrate content of the soil in these countries is also largest in the summer time.

Dhar and Atma Ram (*J. Indian Chem. Soc.*, 1933, 10, 287) have shown that in the photo-oxidation of organic substances, specially the amino-acids and hydroxy compounds, appreciable amounts of formaldehyde are formed. The formaldehyde produced

in the photo-oxidation of organic compounds present in the soil is likely to hinder in the bacterial processes taking place in the soil due to the harmful influence of formaldehyde on micro-organisms and hence the nitrification in the soil due to bacteria will be curtailed by the presence of the formaldehyde, which is a powerful antiseptic and is produced in soil by the oxidation of the organic compounds by air in presence of light.

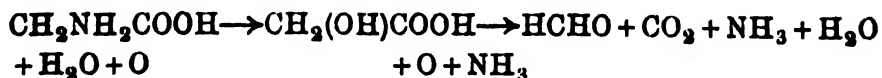
In a private communication to one of the authors, Dr. A. S. Corbet working at the Agricultural Research Station, Bracknell, Berkshire, makes the following statement, "From my experience in Malaya, where I was particularly struck by the paucity of soil micro-organisms, I should think your results on photo-nitrification are of quite general application in tropical countries".

In the unmanured soil of the Institute de Brie-Comte-Robert, Winogradsky found only a few living organisms, three or four kinds of cocci, a few azotobacter, some mycelium of actinomyces and a few yeast but no bacilli or moulds. These are regarded by Winogradsky as the normal population of the soil.

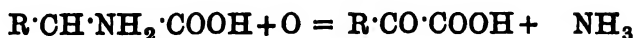
The foregoing observations make it clear that the process of nitrification in soils, specially in tropical countries, is certainly due more to sunlight than to bacteria.

#### *Ammonification—an Oxidation Process.*

In a recent communication (Dhar and Atma Ram, *loc. cit.*), it has been shown that aqueous solutions of amino-acids, like glycine, very readily form formaldehyde and ammonia and carbon dioxide when exposed to air and light:

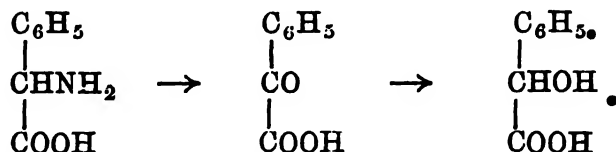


Many years ago Otto Neubauer (*Deut. Archiv. klinische Medizin*, 1909, 95, 211) stated that in the animal body the process of ammonification or *de-amination* might be one of *oxidation* and not *hydrolysis*. The first stage in the process of *oxidative de-amination* can be represented as follows:



The first step in the oxidative de-amination from glycine is expected to be glyoxalic acid and from alanine pyruvic acid  $CH_3COCOOH$ .

That this method of oxidation is actually taking place in the animal body was evident when Neubauer gave phenylglycocoll to a dog and found phenylglyoxalic acid and mandelic acid in the urine.



Phenylglycocoll

Phenylglyoxalic acid

Mandelic acid.

Experiments in progress in these laboratories show the amounts of ammonia obtained on exposing solutions of amino-acids like glutamic acid, aspartic acid etc., to light, increase on passing air through the solutions of amino-acids. These are cases of oxidative de-amination. The formation of ammonia from these amino-acids is greatly increased by the presence of solid surfaces like  $ZnO$ ,  $TiO_2$ ,  $SiO_2$  etc.

It appears that in the soil as well, formation of ammonia from the amino-acids obtained from protein decomposition is, mainly an oxidative de-amination. The amino-acids have been readily oxidised *in vitro* by Palit and Dhar (*cf.* Dhar, "New Conceptions in Biochemistry," 1932) simply by passing air in presence of inductors like ferrous hydroxide, cerous hydroxide, sodium sulphite etc., and on charcoal surface by Warburg. Moreover, aqueous solutions of amino-acids are very easily oxidised by air in presence of light; the oxidation of glycine solutions by air is a highly photosensitive reaction. We are of the opinion, therefore, that the formation of ammonia in the soil is a surface reaction and an oxidation process taking place on the soil surface with liberation of energy. The amino-acids adsorbed on the soil surface are being oxidised to ammonia by the adsorbed oxygen of the air and this chemical change like the process of nitrification in soil can take place even without the presence of bacteria or fungi and is considerably accelerated by light.

This theory easily explains many obscure phenomena taking place in the soil. According to this view point any agency, which

increases either the soil surface or soil temperature or aeration or the amount of light falling on the soil, will lead to increased ammonia formation as well as nitrification.

According to Lathrop (*J. Franklin Inst.*, 1917, 183, 169, 303, 465), histidine, hypoxanthine, cytosine, xanthine, nucleic acid, creatinine, cyanuric acid etc., are of common occurrence in the soil. Marchal (*Bull. Acad. Roy. Sci. Belg.*, 1895, 27, 71) stated that the formation of ammonia from protein is favoured by increase of temperature, complete aeration and a slightly alkaline medium. Moreover, Gainéy (*Soil Sci.*, 1919, 7, 293) reported that insufficient aeration and moisture resulted in a decrease in ammonia formation from dried blood and cotton seed meal. According to Temple (Compare Waksman, "Microbiology", 1927, p. 688), the differences obtained in ammonia formation in different soils are due to a number of causes other than the microbial flora of the soil.

That ammonification in soil is mainly an oxidation reaction is apparent from the statement of Terroin and Wurmser (*Compt. rend.*, 1922, 174, 1435 ; 1922, 176, 228) that a large loss of energy is associated with the process of ammonia formation in soil.

In recent experiments carried on in these laboratories it has been observed that the optimum temperature for bacterial ammonification of urea solutions in presence of soil is 40° ; the velocity of this process at 50° is exceedingly small and stops completely at 55°. Hence in tropical soil, very little of bacterial ammonification of urea is possible in the hot weather, as the soil temperature exceeds 60° in many cases.

In publications from these laboratories (Dhar, "New Conceptions in Biochemistry," p. 100) it has been emphasised that the oxidation of energy-rich substances by air *in vitro* and *in vivo* is markedly accelerated by alkali ; the same behaviour has been observed in the ammonification in soil as stated by Marchal.

#### *An Explanation of Increased Soil Fertility on Partial Sterilization of Soil and on drying it.*

The favourable influence of the drying of soil upon the growth of higher plants is well known. Different soils behave differently in this respect, heavy soils showing greater differences than light soils.

Burning the humus *in situ* sets free plant nutrients and accentuates nitrification. It is stated that in Sweden this step is taken for the regeneration of the soil.

The beneficial effect of fire upon soils has been reported by Worley (*Nature*, 1933, 131, 787) and Topham (*ibid.*, 1933, 132, 102). Similarly partial sterilization of soils leads to their increased fertility. According to Russel and Hutchinson (*J. Agric. Sci.*, 1909, 3, 111; 1913, 5, 152) partial sterilization of soil by heating it to 60° or treatment with volatile antiseptics, increases the rate of oxidation in the soil. Russel ("Soil Conditions and Plant growth", 1932, p. 441) makes the following interesting statement on this point—"The fact has long been known to cultivators of the soil. Heating the soil has been practised from time immemorial in India, the process is called "rab" and is mentioned in the Vedas; the burning of stubble was known by the Romans to increase the fertility of the soil, and various possible explanations were shrewdly put forward by Virgil. Exposure of the soil to the baking heat of the sun is an ancient practice still common in India and in Egypt, where it is known as *sheraqui* and has been studied by J. A. Prescott and shown to be due partly to microbiological and partly to physical causes. Lebedjantzev considers that this repeated drying and heating of the soil plays no small part in maintaining its fertility in hot countries. *The effects on the plant are in all cases described as resembling those of nitrogenous manure*".

"*This increased production of ammonia and nitrate is not a necessary consequence of the higher numbers of organisms ; on the contrary, higher numbers, e.g., those induced by adding non-nitrogenous organic matter to the soil, might depress the ammonia and nitrate content by taking up these substances for their own nutrition. The increased production of ammonia and nitrate is a distinct phenomenon and several explanations have been put forward to account for it.*" Waksman ("Microbiology", 1927, p. 746) states "sterilization by heat results also in the destruction of the nitrifying bacteria ; it brings about a decided increase in the amount of ammonia accumulated in the soil".

"A large number of antiseptics bring about true partial sterilization with the following results :

1. The destruction of the protozoa and nitrifying organisms.

2. An initial increase of ammonia followed by a considerable increase in the rate of ammonia formation and consequently of soil productivity.

3. The complete or almost complete destruction of the soil fungi, of soil nematodes and other soil infesting worms and insects etc".

"It is sufficient to mention, among the volatile antiseptics, toluol, carbon disulphide and chloroform. Concentrations of 1 to 4 per cent of the disinfectant are allowed to act upon the soil for 12 to 48 hours, the soil is then aerated so that the disinfectant may evaporate".

From the foregoing quotations, it will be evident that the increased production of ammonia and nitrate on drying the soil, on heating it or sterilizing it by volatile antiseptics is not due to higher number of organisms in the soil. Hence the protozoan and other existing theories based on microbic action are insufficient to explain this increased soil fertility. The view advanced in this paper can satisfactorily explain this interesting observation based on experience. On drying, on heating and sterilizing with volatile antiseptics, the soil surface and the aeration are increased and hence the oxidation of the amino-acids by atmospheric oxygen leading to the liberation of ammonia and its subsequent oxidation are increased. Moreover, sunlight or diffused day light is always present and is accelerating the formation of ammonia from amino-acids and its oxidation to nitrite. It appears that the increased fertility on heating the soil or exposing it to sunlight as is done by cultivators in many countries is mainly due to increased oxidation of the nitrogenous compounds, mainly the amino-acids, by air causing the formation of ammonia and increased nitrification brought about by making the soil more porous and the accentuation of the air supply and increased soil temperature and above all by the light absorption.

It seems that both ammonification and nitrification in soil are oxidation reactions markedly accelerated by heat and light and both the processes may be actively going on in presence of light even in the absence of bacteria.

According to Maximov ("Plant Physiology", 1930, p. 50), Russian black soils contain 0.5% organic nitrogen, 0.02% ammoniacal nitrogen and 0.003% of nitric nitrogen. The grey forest soils contain 0.25, 0.001 and 0.0008% and the sandy soil, of Leningrad 0.09, 0.002 and 0.0009%.



Wyatt, Ward and Newton (*J. Agric. Sci.*, 1926, 7, 1) have stated that in the case of some soils rich in organic matter, as in the fertile prairie soils, the transformation of ammonia into nitrate is a slower reaction than the production of ammonia, which, therefore, increases in the soil.

It appears that in soils, the processes of ammonification and nitrification go on simultaneously, the velocity of the oxidation of the amino-acids forming ammonia appears to be greater than the velocity of the oxidation of the ammonium salts and ammonia to nitrite and nitrate by air and hence in many soils, the amount of nitric nitrogen present is less than that of ammoniacal nitrogen. Our experimental results obtained on exposing urea solutions and egg-yellow suspensions to light show that the amounts of ammonia formed are always greater than the amounts of nitrite produced. The soil with which our experiments have been performed contained more nitrate than ammonia, perhaps due to the greater oxidation of ammonium salts in presence of sunlight.

Further work on photo-ammonification and nitrification and bacterial count are in progress in these laboratories.

#### SUMMARY.

1. When ammonium salts mixed with sterilized or unsterilized soils are exposed to sunlight in contact with air for 550 hours, the exposure being spread over a year, the amounts of the ammonium salts oxidised to nitrite are as follows:

Ammonium chloride (sterilized soil)	...	...	... 65%.
„ „ (unsterilized soil)	...	...	... 58
Ammonium phosphate (sterilized soil)	...	...	... 55
„ „ (unsterilized soil)	...	...	... 60.2
Ammonium sulphate (sterilized soil)	...	...	... 16
„ „ (unsterilized soil)	...	...	... 28

The oxidation in the dark is much less and lies between 14 to 2%.

2. The amounts of ammonia and nitrite formed on exposing solutions of urea or suspensions of egg-yellow mixed with sterilized or unsterilized soil to sunlight for 224 hours are always greater in light than in the dark. The amounts of ammonia are greater than those of nitrite produced.

3. The optimum temperature for bacterial nitrification in hot countries is 35°, whilst the soil temperature in summer months may

be 70°. Hence nitrification in the summer cannot be appreciably due to bacteria, although the nitrate content of soil is greatest in the summer.

4. The formaldehyde formed in the photo-oxidation of organic compounds present in the soil is likely to exert harmful effect on the bacterial process taking place in the soil.

5. The process of ammonification in soil, that is, the formation of ammonia from the amino-acids obtained from protein decomposition appears to be mainly an oxidative de-amination taking place on the soil surface by the oxygen of air aided by light. Any agency, which increases either the soil surface or soil temperature or aeration or the amount of light falling on the soil, will cause increased ammonia formation as well as nitrification.

6. The increased production of ammonia and nitrate on drying the soil, on heating it or taking it in sunlight or sterilizing it by volatile antiseptics can not be explained from the protozoan and other existing theories based on microbic action, because all these processes lead to a decrease in the number of organisms present in the soil. The soil surface and aeration, however, are increased by these processes and hence the oxidation of amino-acids by atmospheric oxygen leading to the liberation of ammonia and its subsequent oxidation to nitrite are increased, these oxidations being accelerated by light.

7. It appears, therefore, that both ammonification and nitrification in soil are oxidation reactions markedly accelerated by light and heat and both these processes may actively go on in presence of light even in the absence of micro organisms.

Our best thanks are due to Messrs Jagabandhu Mittra, M.Sc. and Rabindranath Ghosh M.Sc. for helping us in the experiments.

**Variation of the Cataphoretic Speeds of Colloidal Particles. Part VI. Further Experiments on the Variation of the Cataphoretic Speeds with Dilution of the Colloidal Solution and in Presence of Added Electrolytes.**

BY JNANENDRANATH MUKHERJEE, SATYAPRASAD ROYCHOU DHURY AND SANTIRANJAN PALIT.

The results published in earlier parts (*J. Indian Chem. Soc.*, 1925, 2, 296; 1927, 4, 493; 1928, 5, 697; 1928, 5, 735; 1933, 10, 27) show on the one hand that the prevalent conception of the relation between the stability of a colloid and a critical coagulating potential, or, of the factors affecting the cataphoretic speed are unsatisfactory, and on the other hand that the variations in the cataphoretic speed with dilution of the sol, addition of electrolytes and non-electrolytes are of a very complicated nature. These measurements have helped us to some extent to understand the peculiarities of the factors affecting the cataphoretic speeds, such as the adsorption of ions, the distribution of the ions in the double layer and the state of aggregation. Thus Mukherjee, Roychoudhury and Biswas (*J. Indian Chem. Soc.*, 1931, 8, 381) have shown that various types of curves are obtained in the dilution of ferric hydroxide sol (cf. also S. N. Mukherjee, *Kolloid Z.*, 1930, 52, 63). With arsenious sulphide sol also, the speed-dilution curve depends on the specific nature of the sol. Working with ferric hydroxide sol and potassium chloride solutions, the above authors have found a considerable drop in the cataphoretic speed after coagulation of the sol with progress of time. Also it has been shown (Part V) that the order of decrease of the cataphoretic speed of arsenious sulphide sol by NaCl, KCl and LiCl is  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ , which is contrary to previous observations as also to the order of coagulating concentrations of these electrolytes.

In view of the multifarious types of results obtained which showed that the variation of the cataphoretic speed depended on the specific nature of the colloid, it was thought desirable to carry out our further experiments. The present paper deals with the cataphoretic speeds of (1) arsenious sulphide, silicic acid and aluminium hydroxide sols with the dilution of the sol; (2) aluminium hydroxide sol mixed with potassium chloride and potassium sulphate solutions; (3) ferric hydroxide sol mixed with potassium chloride, potassium sulphate, sodium chloride and lithium chloride solutions.

#### EXPERIMENTAL.

##### *Preparation of Sols.*

(1) *Arsenious sulphide sol.*—The method of preparation of the sol was as described previously (Part II, *loc. cit.*, p. 497).

*Ferric hydroxide sol.*—The method of preparation was as described in Part IV, p. 736. The sol was dialysed against repeated changes of hot distilled water until the dialysate was nearly free from chloride (a period of about a month).

(3) *Silicic acid sol (samples A, B<sub>1</sub>, B<sub>2</sub> and C).*—210 C.c. of Kahlbaum's concentrated hydrochloric acid (*pro analyse*) was diluted with 700 c.c. of conductivity water. In it, 525 c.c. of sodium silicate solution of 1.16 sp. gr. was added in a thin stream with continuous stirring. Then the sol was allowed to dialyse in a parchment bag against repeated changes of cold distilled water until a slight opalescence was obtained (a period of 6 days). The sol was kept stocked in the atmosphere of hydrogen (A).

Another sample was prepared in the same way as sol A but 1.7 times more dilute. A portion was taken out after dialysis for 10 days (B<sub>1</sub>) and another portion after dialysis for one week more (B<sub>2</sub>). Sample C was prepared in the same way as sample A, but dialysed in a current of running distilled water for 2 days. This sample was very unstable, setting rapidly to a gel in a few days.

(4) *Aluminium hydroxide sol (sample A).*—The aluminium hydroxide sol was prepared by adding slightly less than the equivalent amount of ammonium hydroxide solution (N/10) slowly and with vigorous stirring to a solution of aluminium chloride (N/10). The resulting sol was purified by dialysis in a parchment bag against repeated changes of distilled water, until a turbid sol was obtained.

*Procedure.*

Cataphoretic speeds at  $35 \pm 0.5^\circ$  were measured by using two separate U-tubes having effective distance of 4.01 cm. and of 2.89 cm. respectively. The former was used for work with arsenious sulphide, ferric hydroxide (A), silicic acid and partly with aluminium hydroxide sols, while the latter tube was used for all other measurements. The difference in viscosity being small, the speed has not been corrected for its variations. Some of the measurements were carried out in duplicate to find the reproducibility of the results.

During the measurements considerable difficulties were experienced in many cases. The difficulties have been described in a separate paper. The present paper records only reliable and reproducible data.

*Variation of Cataphoretic Speeds with Dilution of Sols.*

*Measurements with arsenious sulphide sol.*—In conformity with previous measurements, an equiconducting solution of hydrochloric acid was used as upper liquid. The colour contrast for reading the position of the boundary and produced by a deep blue glass filter, in previous measurements with this sol, was found to be insufficient. A layer of dilute permanganate solution contained in a rectangular absorption vessel and interposed in the path of the light was found quite satisfactory. The sol appeared purple while the colourless upper liquid appeared violet. With the diluted sols another difficulty was met with. The potential gradient was repeatedly observed to be very high when the circuit of the potentiometer was first closed and gradually dwindled down to a minimum limiting value in an hour or more. With the sol diluted 1 to 20 a constant potential gradient was not even approximately attained. Moreover, at this dilution the upward speed was very small in comparison with the downward one. The more diluted sols showed a tendency to settle. The results are given in Table I and Fig. 1, curve 1.

TABLE I. (Fig. 1, curve 1).

Sp. conductivity of the undiluted arsenious sulphide sol  
 $= 2.05 \times 10^{-6}$ .

$p_H$  of the supernatant liquid of the undiluted sol after coagulating it with  $KCl=6.16$ .

Dilution with equal vol. of water,	Direct Pot. gradient		Rate of migration $\times 10^5$ .	Reverse Pot. gradient		Rate of migration $\times 10^5$ .	Mean rate of migration $\times 10^5$ .
	Before.	After.		Before.	After.		
Undiluted sol	0.542	0.552	59.6	0.534	0.520	61.9	60.7
	0.580	0.558	58.5	0.540	0.546	62.6	
1:1	0.598	0.691	66.3	0.616	0.610	61.0	65.5
	0.556	0.558	68.8	0.570	0.578	66.0	
1:5	0.694	0.619	55.3	0.624	0.624	58.8	58.1
	0.696	0.625	52.0	0.637	0.640	59.4	
1:10	0.662	0.652	67.8	0.704	0.689	63.3	67.0
	0.600	0.600	68.4	0.653	0.652	69.0	

Measurements on the effect of the dilution on the cataphoretic speed of arsenious sulphide sol (Mukherjee, *Proc. Roy. Soc.*, 1923, A 108, 102; also Parts II and III) are given in Fig. 1, curves 2, 3 and 4.

FIG. 1.

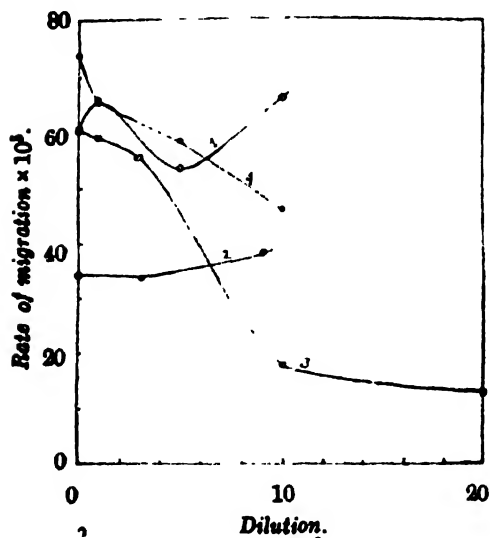
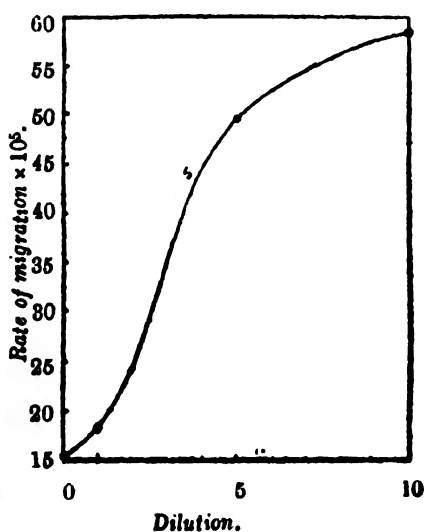


FIG. 2.



One finds that the variation of the cataphoretic speed with dilution depends on the sample of sol worked with. Curve 2 shows that the speed is not materially affected by the dilution. Curves 3 and 4 show a continuous decrease at all dilutions and curve 1 is rather peculiar having a S-shape. These peculiarities in behaviour cannot be reconciled with the theoretical point of view which regards colloidal arsenious sulphide to behave as an electrolyte, *vis.*, a weak acid. There is no parallelism between the variation of the mobility of an

anion of an acid with the dilution of the acid and that of the cataphoretic speed of the colloidal particles of the arsenious sulphide sols. According to this point of view the mobility should continuously increase with the dilution. Apparently the valencies and the numbers per unit surface of the primarily adsorbed ions, which together determine the surface density of the electric charge and the distribution of the ions in the double layer determine the cataphoretic speed. The adsorption of ions as opposed to surface dissociation offers the only rational theoretical basis for an elucidation of these variations.

*Measurements with silicic acid sols.*—This sol as prepared here tends to set as a gel (occasionally in the dialyser itself) and in most cases can hardly be stocked for more than one or two weeks. A solution of hydrochloric acid of equal  $p_H$  as the sol and made equiconducting with the sol by the addition of a few drops of a concentrated solution of  $\text{Na}_2\text{SiO}_3$ , has been used as the upper liquid. Equiconducting HCl solution has also been tried with no better advantage than the above mixture. It is also desirable to use a mixture of HCl and  $\text{Na}_2\text{SiO}_3$  which is both equiconducting and has the same  $p_H$  as the sol. A peculiarity observed with this sol is that sometimes a certain length near about the boundary or the whole of the sol sets to a gel in the tube. The gel formation is hastened on passage of current through the sol. The boundary of the gel moves without any apparent separation of the gel near the boundary from its main body. The cataphoretic speed of this sol varies greatly from sol to sol and is smaller than that of the usual suspensoid sols.

TABLE II.  
Silicic acid sols.

Sol.	Upper liquid.	Upward movement.						Mean of rate of migration $\times 10^6$ .	
		$pH$	Pot. gradient		Rate of migration $\times 10^6$ .	Pot. gradient			Rate of migration $\times 10^6$ .
			Before. After.			Before. After.			
			Before.	After.		Before.	After.		
A*	HCl of equal $p_H$ & $\text{Na}_2\text{SiO}_3$	1.9	0.714	0.612	12.6	0.496	0.557	17.94	15.27
B <sub>1</sub> *	HCl	2.5	0.558	0.508	Very small	0.558	...	Very small	Very small
B <sub>1</sub> /2**	HCl & NaCl	2.88	1.08	1.13	8.1	1.18	1.08	2.1	2.6
B <sub>2</sub> **	"	3.17	1.61	1.59	13.47	1.48	1.41	17.36	15.41
C**	"	3.4	1.45	1.43	7.7	1.46	1.4	4.5***	6.1

\* Effective distance of the U-tube used was 4.01 cm.

\*\* Effective distance of the U-tube used was 2.89 cm.

\*\*\* The sol sets to a jelly.

It has been reported in a paper recently communicated to this Journal that a mixture of HCl of the same  $p_H$  as the sol and  $\text{Na}_2\text{SiO}_3$  serves as a suitable upper liquid for silicic acid sol. But Table III shows that for sol A, a mixture of HCl and  $\text{Na}_2\text{SiO}_3$  does not give a constant potential gradient and moreover, a considerable rate of settling of the sol is observed. In the later part of our work we found that a mixture of NaCl and HCl as upper liquid gives a more satisfactory potential gradient. Sol A had already become very thick and showed signs of gel formation and it was not possible to take measurements using the above mixture as upper liquid. It is, however, interesting that both the upward and downward cataphoretic speeds increase on dilution of the sol. The measurements of cataphoretic speeds in Table III, therefore, although not satisfactory, enable us however to draw qualitative conclusions.

TABLE III. (Fig. 2, curve 5).

*Silicic acid sol (A)*

Dilution with equal vol of water.	Sp. conducti- vity.	$p_H$ .	Pot. gradient		Rate of migra- tion $\times 10^5$ .	Pot. gradient		Rate of migra- tion $\times 10^5$ .	Mean of rate of migra- tion $\times 10^5$ .
			Before.	After.		Before.	After.		
Conc. sol	0.005700	1.9	0.714	0.612	12.61	...	...	...	...
			0.612	0.547	5.75	0.496	0.557	17.94	15.27
			0.547	0.482	4.23	0.657	0.635	19.34	...
1:1	0.00288	2.3	0.687	0.613	16.24	0.605	0.568	20.84	18.54
			0.634	0.605	17.11	0.612	0.576	18.60	12.90
1:5	0.001047	2.4	0.678	0.618	21.79	0.693	0.553	78.65	50.22
			0.670	0.663	21.72	0.670	0.574	77.67	49.49
1:16	0.000484	3.0	0.559	0.588	22.1	0.888	0.829	98.90	57.54
			0.647	0.681	22.59	0.691	0.559	91.69	58.64
1:1 *			0.703	0.703	3.95	...	...	...	...
			0.702	0.671	1.03	0.646	0.571	10.06	7.05

The potential gradient varies as much as 15%. This indicates ionic migrations and possibly interactions at the boundary which change the concentration of the electric carriers and the specific conductivities. The cataphoretic speeds gradually increase with the dilution.

\* A HCl solution of the same  $p_H$  as the silicic acid sol was made equiconducting as the sol by the addition of NaCl solution. The sol, however, had become very thick and showed signs of gel formation.



The  $H^+$  ion and  $Cl^-$  ion concentrations of these sols were measured by Mr. B. R. Majumdar and decrease with the dilution. As however the ideal conditions in the measurement of cataphoretic speeds could not be attained, it is not profitable at this stage to try to correlate the variation of the cataphoretic speed with the observed variations of absorbed  $H^+$  and  $Cl^-$  ions on the surface of colloidal particles of silicic acid sol.

*Aluminium Hydroxide Sol (Sample A) mixed with Electrolytes.*

A slow rate of filling the tube is necessary in order to secure a sharp boundary. The opalescence of these sols is very weak and in order to ensure that the boundary can be seen to rise at the desirable rate the cathetometer was focussed on the upper meniscus of the upper liquid and the stop-cock was gradually opened until a slow motion of the meniscus was perceived in the cathetometer. With practice a sharp boundary can be obtained.

Attempts to measure the cataphoretic speeds of  $Al(OH)_3$  sols (K and L) were unsuccessful. These sols had low specific conductivities (about  $3 \times 10^{-5}$ ) and the  $p_H$  values were about 7.0. With one sample (L) it was possible to produce a definite boundary but as soon as the current was switched on, the sol rose upwards in streaks. Sometimes a more or less ill-defined boundary was formed which broke up again during the migration.

TABLE IV (Fig. 8, curves 6 & 7).

*Aluminium hydroxide sol (A).*

Dilution with equal vol of water.*	Sp. Conduc- tivity.	$p_H$ .	Pot. gradient		Rate of mi- gration $\times 10^5$ .	Pot. gradient		Rate of mi- gration $\times 10^5$ .	Mean rate of mi- gration $\times 10^5$ .
			Before.	After.		Before.	After.		
Conc.	0.0009249		0.531	0.531	49.25	0.561	0.561	46.5	47.8
			0.592	0.57	44.5	0.607	0.607	50.8	—
1:1	0.0003327	4.05	0.561	0.558	50.87	0.575	0.600	51.6	50.98
1:5*	0.000293		0.627	0.630	41.32	0.620	0.627	62.95	52.1
1:10	0.0001175		0.617	0.612	52.67	0.627	0.634	52.9	52.78

\* At this dilution the boundary showed an initial erratic movement for a comparatively long time. In order to avoid this error, all the readings have been taken after the current has been allowed to flow for 10 minutes and then without switching off the current.

FIG. 3.

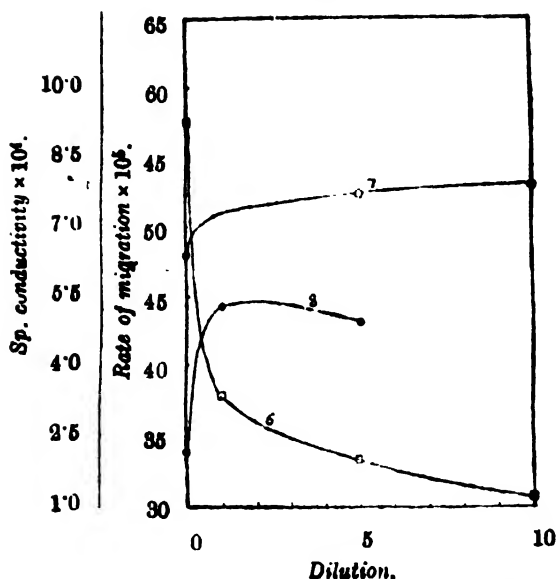


FIG. 4.

Conc. of Electrolyte in normality  
(curve 11).

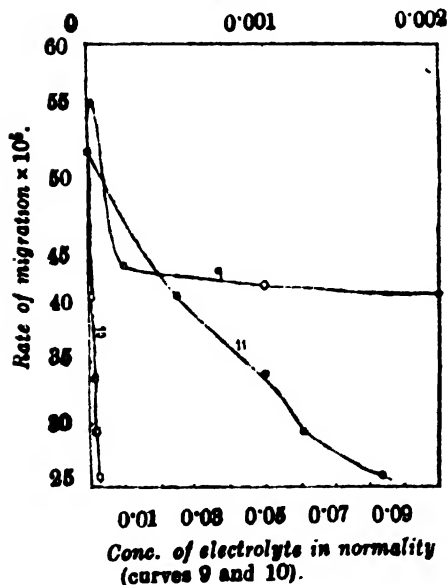


FIG. 5.

Conc. of electrolyte in normality  
(curve 17).

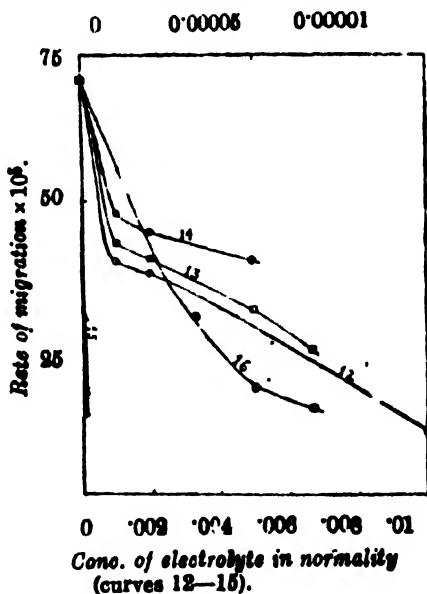


Fig. 3, curves 6 and 7 represent respectively the specific conductivities and the cataphoretic speeds against the dilution and curve 8 in the same figure represents the variation of the cataphoretic speed of another aluminium hydroxide sol (*cf.* Mukherjee, *J. Phys. Chem.*, 1962, 36, 688).

With sol A, the specific conductivities decrease while the cataphoretic speed increases with the dilution. For curve 8 there is an initial increase (at dilution 1:1) and then tends to decrease somewhat.

The cataphoretic speeds of aluminium hydroxide sols with increasing concentrations of potassium chloride and sulphate are given in Tables V and VI.

TABLE V (Fig. 4, curve 9).

 $\text{Al}(\text{OH})_3$  sol (A) and KCl.

Conc. of electrolyte in normality	Upward movement.		Rate of migration $\times 10^5$ .	Downward movement.		Mean rate of migration $\times 10^5$ .
	Pot. gradient			Pot. gradient		
	Before.	After.		Before.	After.	
0	1.311	1.811	52.07	1.38	1.37	53.09
0.001*	0.561	0.553	50.87	0.675	0.600	51.06
0.001*	0.590	0.584	55.35	0.576	0.620	55.62**
0.01*	0.635	0.618	41.93	0.642	0.627	42.98**
0.05	1.356	1.387	41.18	1.407	1.356	—**
0.10	1.811	1.833	40.3	1.38	1.307	49.82***

\*A different cataphoretic tube was used for the measurements.

\*\*Within a few minutes of the downward movement, the boundary separated into two layers, a thin above a thick one. On reversing the movement, the two boundaries coalesced and this phenomenon could be again repeated a number of times. The readings were always taken on the upper layer.

\*\*\*Flocculated during the latter part of the movement, so the value is possibly affected by the gravitational fall of the bigger particles.

TABLE VI (Fig. 4, curves 10 and 11).

 $\text{Al}(\text{OH})_3$  sol (A) and  $\text{K}_2\text{SO}_4$ .

Conc. of electrolyte in normality.	Upward movement.		Rate of migration $\times 10^5$ .	Downward movement.		Mean rate of migration $\times 10^5$ .
	Pot. gradient			Pot. gradient		
	Before.	After.		Before.	After.	
0		Vide TABLE VI				51.77
0.0005.	0.0617	0.682	36.03	0.617	0.588	44.26
0.001	1.344	27.49	27.49	1.413	1.413	41.68
	1.414	1.475	28.00	1.516	1.465	38.34
0.000125	1.354	1.375	29.5	1.435	1.445	28.93
	1.375	1.415	37.87			
0.00166	1.344	1.354	19.73	1.364	1.364	32.58*
						26.13

\*Flocculates. There is a noticeable difference between upward and downward cataphoretic speeds.

For 0.001*N*-potassium chloride the speed shows an increase but decreases at higher concentrations up to 0.1*N* (coagulating region, curve 9). With  $K_2SO_4$ , however, there is a continuous decrease. Fig. 4, curve 11 represents curve 10 on a magnified scale. As is to be expected the decrease of the speed is much greater with  $K_2SO_4$  than with KCl. The cataphoretic speeds at the coagulating region differ considerably for the two electrolytes and show that the assumption of a critical coagulation potential is not justifiable.

*Ferric Hydroxide Sol mixed with Electrolytic Solutions.*

This sol is very sensitive towards electrolytes. The tube after the usual cleaning with hot chromic acid solution can only be used after it has been kept filled with conductivity water for a few hours. The liquid used in calomel vessels for measuring the potential gradient at the boundary. As a result the movement of the boundary gradually slows down sometimes accompanied by slight haziness at the boundary. This can be avoided by proper care. The results are given in Tables VII, IX, and X, Fig. V.

TABLE VII (Fig. 5, curve 12).

$Fe(OH)_3$  sol and KCl.

Conc. of electrolyte in normality.	Upward movement.			Downward movement.			
	Potential gradient		Rate of migration $\times 10^5$ .	Potential gradient		Rate of migration $\times 10^5$ .	Mean rate of migration $\times 10^5$ .
	Before.	After		Before.	After.		
0.30	1.746	1.867	59.28	1.746	1.603	82.94	71.08
0.001*	1.391	1.452	32.84	1.451	1.411	45.74	39.29
0.002*	1.364	1.401	31.34	1.431	1.411	48.89	37.36
0.01†	1.36	1.401	10.86	1.401	1.421	—	10.86(?)

\* A sudden drop in the potential gradient on the addition of the electrolyte is observed. This has been dealt with in a separate paper.

† Complete flocculation took place.

TABLE VIII (Fig. 5, curve 18):

 $\text{Fe}(\text{OH})_3$  sol and NaCl.

Conc. of electrolyte in normality.	Upward movement.			Downward movement.			
	Potential gradient		Rate of migration $\times 10^5$ .	Potential gradient		Rate of migration $\times 10^5$ .	Mean rate of migration $\times 10^5$ .
	Before.	After.		Before.	After.		
0	1.746	1.867	59.23	1.746	1.603	82.94	71.08
0.0011	1.409	1.409	35.48	1.413	1.368	55.16	42.68
	0.98	1.01	33.5	0.966	0.966	46.59	
0.0025	1.409	1.429	35.31	1.389	1.452	43.61	40.16
0.0056	1.425	1.429	24.52	1.378	1.338	38.06	31.29
0.00667	1.419	1.413	24.72	1.051	0.6534	—	24.72

TABLE IX (Fig. 5, curve 14).

 $\text{Fe}(\text{OH})_3$  sol and LiCl.

Conc. of electrolyte in normality.	Upward movement.			Downward movement.			
	Potential gradient		Rate of migration $\times 10^5$ .	Potential gradient		Rate of migration $\times 10^5$ .	Mean rate of migration $\times 10^5$ .
	Before.	After.		Before.	After.		
0	1.746	1.867	59.23	1.746	1.603	82.94	71.09
0.001*	1.006	1.317	34.88	1.416	1.374	57.38	47.65
	1.386	1.416	36.88	1.372	1.386	61.55	—
0.002†	1.374	1.403	28.81	1.374	1.342	60.15	44.48
0.005‡	2.355	1.868	24.58	1.311	1.295	55.0	39.70

\* A sudden drop in the potential gradient on the addition of electrolyte is observed. This has been dealt with in a separate paper.

† Complete flocculation took place.

‡ The sol became hazy and coagulated partially within a few minutes.

TABLE X (Fig. 5, curves 15 and 16).

 $\text{Fe(OH)}_3$  sol and  $\text{K}_2\text{SO}_4$ .

Conc. of electrolyte in normality.	Upward movement.			Downward movement.			
	Potential gradient		Rate of migration $\times 10^5$ .	Potential gradient		Rate of migration $\times 10^5$ .	Mean rate of migration $\times 10^5$ .
	Before.	After.		Before.	After.		
0	1.746	1.867	59.23	1.746	1.603	82.94	71.08
.000088*	1.389	1.419	21.37	1.419	1.41	40.05	30.71
.00005†	1.951	1.491	16.79	1.512	1.451	16.83	
	1.491	1.491	16.77	1.461	1.501	19.57	17.54
.000058†	1.355	1.387	13.38	1.396	1.355	14.48	13.98

Fig. 5, curve 15 has been shown in curve 16 on a magnified scale in the same figure. In all cases, the cataphoretic speed of the sol continually decreases with the concentrations of the electrolyte. Unlike the case of aluminium hydroxide sol, no initial increment of the cataphoretic speed of the sol at very low concentrations of potassium chloride has been observed in this case. The above data also show that a critical coagulation potential does not exist.

## SUMMARY.

1. The speed-dilution curve of arsenious sulphide sol is S-shaped in form. This peculiar behaviour cannot be reconciled with the theoretical point of view which regards colloidal arsenious sulphide to behave as an electrolyte, *viz.*, as a weak acid..

2. The cataphoretic speeds of silicic acid sols vary greatly from sol to sol and is smaller than that of the usual suspensoid sols. Sometimes a certain length near about the boundary or the whole of the silicic acid sol sets to a gel in the tube. The gel formation is hastened on passage of current through the sol.

The cataphoretic speeds of silicic acid sol (A) increase on dilution of the sol.

\* A sudden drop in the potential gradient on the addition of electrolytes is observed. This has been dealt with fully in a separate paper.

† Partial coagulation took place.

3. The cataphoretic speeds of aluminium hydroxide sol (A) increases on the dilution of the sol. The specific conductivity of the sol, however, decreases with dilution.

4. With sample (A) of aluminium hydroxide sol, the cataphoretic speed increases at 0.001N-KCl but decreases at higher concentrations up to 0.1N (Coagulation region). With  $K_2SO_4$  however there is a continuous decrease. The cataphoretic speeds at the coagulation region differ considerably for the two electrolytes and show that the assumption of a critical coagulation potential is not justifiable.

5. Measurement of cataphoretic speeds of ferric hydroxide sol in contact with KCl,  $K_2SO_4$ , NaCl continually decrease with increasing concentrations of the above electrolytes. These observations also show that a critical coagulation potential does not exist.

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*Received September 15, 1938.*

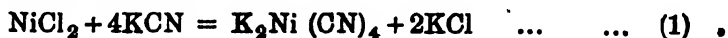




## Potentiometric Study of the Quinhydrone Electrode in the Estimation of Nickel.

By B. K. CHATTERJEA AND J. B. JHA.

Moore (*Chem. News*, 1895, 72, 92) devised a method for the volumetric estimation of nickel salts in solution. The reaction on which the method depended was



To a measured volume of an ammoniacal nickel solution was added an excess of potassium cyanide. The excess of the cyanide was then titrated with silver nitrate solution using potassium iodide as an indicator. On the basis of the method Müller and Lauterbach (*Z. anal. Chem.*, 1922, 61, 457) carried on a potentiometric titration. A potential jump against silver electrode was observed as soon as all the nickel was transformed into the complex ion  $\text{Ni}(\text{CN})_6$ . The method did not yield correct results owing to the potential jump being very small at the end-point. An absolute method of the determination of the end-point was then investigated by Müller and Schluttig (*Z. anorg. Chem.*, 1924, 134, 827) by titrating directly with standard potassium cyanide solution. A potential break was found at a point corresponding to the complex ion formation,  $\text{Ni}(\text{CN})_4$ . Owing to the slow transformation of the precipitated nickel cyanide  $\text{Ni}(\text{CN})_2$  into potassium nickelocyanide,  $\text{K}_2\text{Ni}(\text{CN})_4$  there is a great chance of under titration and the results yielded an error of about 7%. Afterwards they titrated nickel solutions by opposing an inflectional potential of -253 volts to that of the cell against normal calomel electrode. An effective stirring and rapid titration was essential in the process of titration.

From the above it is evident that the slow transformation of the precipitated nickel cyanide into the complex salt introduces complications and even in the absolute method of Müller and Schluttig (*loc. cit.*) there is a great chance of over titration giving rise to the positive error. The aim of the following experiments is to locate the end-point correctly at a point when the nickel is completely precipitated as  $\text{Ni}(\text{CN})_2$  and the complex salt just begins to form.

The reaction (1) may be represented as (i) the formation of nickel cyanide which being insoluble is precipitated as

$\text{Ni(A)}_2 + 2\text{KCN} = \text{Ni(CN)}_2 + 2\text{KA}$  where A represents an univalent anion;

(ii) the formation of the complex salt  $\text{K}_2\text{Ni(CN)}_4$  as



If the end-point can be detected at the completion of the reaction (1), the error due to the slow transformation of  $\text{Ni(CN)}_2$  to  $\text{Ni(CN)}_4$  will be easily eliminated. The applicability of the quinhydrone electrode will be clear from the following theoretical considerations.

All salts of weak bases and strong acids give an acid reaction. The hydrogen ion concentrations of their solutions is given by,

$$p_H = 7 - \frac{1}{2} p_b - \frac{1}{2} \log C$$

where,  $C$  = concentration of the salt, and  $p_b = -\log K_b$  and  $K_b = \frac{(\text{B}^+) \times (\text{OH}^-)}{(\text{BOH})}$ .

The hydrogen ion concentration of nickel salts of mineral acids falls under this class and therefore at the completion of the  $\text{Ni(CN)}_2$  formation, the hydrogen ion concentration will be nearly, but not equal to nor greater than,  $10^{-7}$ . (In this consideration, the effect of substances formed during titration has been neglected, although a further consideration will reveal that the effect is not negligible.) When a slight excess of potassium cyanide is added, the complex salt  $\text{K}_2\text{Ni(CN)}_4$  is formed and the  $p_H$  value is given by,

$$p_H = 7 + \frac{1}{2} p_a + \frac{1}{2} \log C.$$

Neglecting  $C$  which is very small at the end-point, the change in hydrogen ion concentration is from,  $7 - \frac{1}{2} p_b$  to  $7 + \frac{1}{2} p_a$ . The actual change in *e.m.f.* due to corresponding changes in hydrogen ion concentration will therefore depend upon the values of  $K_b$  and  $K_a$  as well as on the relative strength of the solutions.\*

The abrupt change in *e.m.f.* was seen by a preliminary series of titrations at the point where  $\text{Ni(CN)}_2$  was completely precipitated.

#### EXPERIMENTAL.

*The apparatus.*—The apparatus used was of a very simple nature. An accumulator with a variable resistance in series was used along

\* Depending upon the variation in hydrogen ion concentration, Rupp and Pfennig (*Chem. Ztg.*, 1910, **34**, 322-323) titrated a neutral solution of nickel with KCN till the point corresponding to the complex ion formation. They used phenolphthalein as an indicator (*pH* 9.8).

with the ordinary wire bridge potentiometer (made and calibrated by W. G. Pye & Co., Cambridge). The variable resistance was adjusted till a voltmeter placed across the terminals of the potentiometer read exactly one volt. As only changes in *e.m.f.* were to be observed no standard cell was used, although care was taken to see that the current of the secondary cell was constant during the time of the experiment.

*Standardisation of potassium cyanide solution.*—Potassium cyanide solutions were prepared by dissolving an approximately weighed amount of the salt in a particular volume of distilled water. The solutions were standardised by nickel solutions containing a known amount of nickel in it. The standardisation was necessary in the case of KCN solutions because even the purest sample of KCl available contained sodium salts and moisture.

*Estimation of nickel in nickel solutions.*—Nickel was estimated by electro-analysis in the solutions meant by standardisation as well as those for titrations in order to determine the percentage of error in each titration. Sand's platinum wire gauze electrodes with rotating cathodes were used. A current of 2 amperes reduced to  $1\frac{1}{2}$  amperes towards the end of the analysis was found sufficient to precipitate 0.2 g. of nickel in 30-35 minutes.

Nickel nitrate (which was used for all the titrations) was first converted to nickel sulphate and then made strongly ammoniacal before starting the analysis. In order to prevent the precipitation of nickel in the form of oxide on the cathodes, 2 c. c. of strong ammonia solution was added twice during analysis. The mean of three nearly concurrent readings was taken to represent the actual nickel content. The accuracy of the method and experiments can be judged from the following actual determinations.

		Solution I.	Solution II.
1st determination.	Quantity of Ni per 25 c.c. of soln.	0.1166 g.	0.1444 g.
2nd	do	0.1167	0.1446
3rd	do	0.1150	0.1441
	Mean	0.1161	0.1443

For the purpose of the following titrations pure nickel nitrate (B. D. H., Analytical Reagent) free from cobalt and iron was used. It was intended to study the effect of impurities at a later stage, once the accuracy of the method has been established.

From theoretical considerations it is easy to see that nickel sulphate and nickel chloride would behave in a way similar to nickel nitrate. Some of the results of titrations are as follows.

Solution No. I. Volume of nickel nitrate taken = 25 c.c.

Volume of KCN solution added.	<i>e.m.f.</i> observed against 0.1 <i>N.</i> calomel electrode.	$\frac{dE}{dC}$ .	Volume of KCN solution added.	<i>e.m.f.</i> observed against 0.1 <i>N.</i> calomel electrode.	$\frac{dE}{dC}$ .
0.0 c.c.	+0.1294 volts.		0.6 c. c.	-0.0924 volts	465
15.0	-0.0489		0.8	-0.1017	400
18.0	-0.0676		20.0	-0.1101	365
19.0	-0.0795		0.2	-0.1174	355
0.2	-0.0823	190	0.4	-0.1245	
0.4	-0.0866	290			

$\frac{dE}{dC}$  maximum at 19.7 c.c. of KCN.

1 c.c. of KCN solution = 0.01738 g. of nickel.\*

19.7 c.c. of KCN = 25 c.c. of nickel nitrate solution.

### Results.

Amount of nickel in 25 c.c. of solution found by electroanalysis	...	0.8432
do. by titration	...	0.8426
Error	...	0.2

The results of the above and four other experiments are summarised below for comparison.

Quantity of Ni in 25 c.c. of Ni solution as found by electro-analysis.	as found by titration.	Errors.
1. 0.8432 g.	0.8439 g.	-0.1 %
2. 0.8055	0.8066	+0.3
3. 0.1451	0.1441	-0.6
4. 0.1792	0.1791	-0.06
5. 0.0900	0.08952	-0.6

\* As found by standardisation by a previous titration

*Titration of nickel nitrate solution with caustic soda.*

(Use of Quinhydrone electrode).

Volume of nickel nitrate taken = 25 c.c.

Vol. of NaOH soln. added.	e.m.f. observed against 0.1N. calomel electrode + 1.013.	$\frac{dE}{dC}$	Vol. of NaOH soln. added.	e.m.f. observed against 0.1N. calomel electrode + 1.033.	$\frac{dE}{dC}$
0.0 c.c.	+ 0.0944 volts		21.0 c.c.	- 0.1058 volts	467
5.0	- 0.0278		22.0	- 0.1525	471
10.0	- 0.0465		23.0	- 0.2296	628
15.0	- 0.0605		24.0	- 0.2924	414
20.0	- 0.0920	138	25.0	- 0.3338	

$\frac{dE}{dC}$  maximum at 21.7 c.c. of NaOH solution Strength of NaOH soln. = 0.98N.

*Results.*—Nickel precipitated at end-point is 80%. Hence a basic complex is formed having the probable composition,  $\{\text{Ni}(\text{OH})_2\}_4\text{Ni}(\text{NO}_3)_2$ .

In all the above tables only the final titrations are given. Each titration has been repeated several times to test the concurrency of the method.

From the results, *i.e.*, the nature of titration and maxima it is evident that the titration is similar to that of a weak acid with strong alkali and the end-point lies between  $p_H$  7 and  $p_H$  8.

The above principle was also applied in the titration of nickel salts with caustic soda but the sudden rise in  $p_H$  beyond 8, when about 80% of the nickel has been precipitated as hydroxide, prevented us from following it further. The sudden change in the direction of the curve points to the formation of some basic compound with nickel nitrate. This was also observed by Britton with nickel chloride (Britton, *J. Chem. Soc.*, 1925, p. 2110). Our results point, however, to the formation of the complex salts,  $\{\text{Ni}(\text{OH})_2\}_4\text{Ni}(\text{NO}_3)_2$ .

## CONCLUSION.

The results of the potentiometric titration (using a quinhydrone electrode) of pure nickel salt (nickel nitrate) with KCN point to a sudden change in *e.m.f.* at a point corresponding to the formation of  $\text{Ni}(\text{CN})_2$ . This change is characteristic of weak acids and can be utilised to titrate nickel successfully. The end-point lies between  $p_H$  7 and  $p_H$  8, which is the case in the titration of weak acids against strong alkalis. It is not possible to titrate nickel by caustic soda because a basic compound is precipitated when about 80% of the nickel has been precipitated as hydroxide.

This method of estimating nickel has the following advantages: In the first place, it does not require any absolute measurements. Only changes in *e.m.f.* during titration need be noted. In the second place, it has the advantage of the titration being finished quickly. The apparatus is also simple and does not require any special care. In fairly concentrated solutions *i.e.*, in solutions containing 0.34 to 0.17 g. of Ni in 25 c.c. of the solution, there is no chance of missing the end-point and the errors are well within experimental magnitudes.

The following are the best conditions under which the above method yields good results.

1. *The concentration of the nickel solution should be moderate* (0.34 to 0.09 g./25 c.c.) As the solution becomes more and more dilute it takes a longer time for the potential to be attained and hence a longer time to finish the titration. Also the changes in *e.m.f.* per unit volume of titer added are small and hence a sharp maximum of  $(dE/dC)$  is not obtained.

2. *Stirring.* No stirring device is necessary. As soon as the titer is added into the beaker, it is sufficiently shaken to ensure thorough mixing and then allowed to rest. When the solution is perfectly still, the *e.m.f.* is measured as usual.

3. *The Electrodes.* For quinhydrone electrode moderately thin platinum wires fused in pyrex glass tubes should be used. The platinum wire should not be bent during titration, for a change in the surface strains causes a change in the observed *e.m.f.* When thick wires are used for this purpose the electrodes should be frequently examined to see that no crack exists at the joint and a cracked electrode should be rejected.

## POTENTIOMETRIC STUDY OF THE QUINHYDRONE ELECTRODE 733

The calomel electrode should end in a glass capillary.

4. *The galvanometer.* The galvanometer used should be very sensitive and should give a marked deflection for even very feeble currents, and the lamp and scale method of noting the deflections should be adopted. In the above experiments the author used an Ayrton Mathew galvanometer (Cambridge Instrument Co. Ltd.) and it was quite sensitive. It gave a deflection of 475 mm. for 1 micro-ampere when the scale was at a distance of one meter from the galvanometer.

5. *The accumulator* which supplies current to the potentiometer wire should give a perfectly constant current, i.e., the *e.m.f.* should not change during the process of titration. Even a very small change is likely to cause serious error in the observed *e.m.f.* In the above experiments, a hundred (100) amp. hour oxide battery was used when the *e.m.f.* between the two ends was 2.0 volts, for the *e.m.f.* is not steady when above this voltage.

6. A thorough insulation of all the connecting wires is absolutely essential. The above experiments were performed by using a high quality flexible chords (Rubber and Silk insulated).





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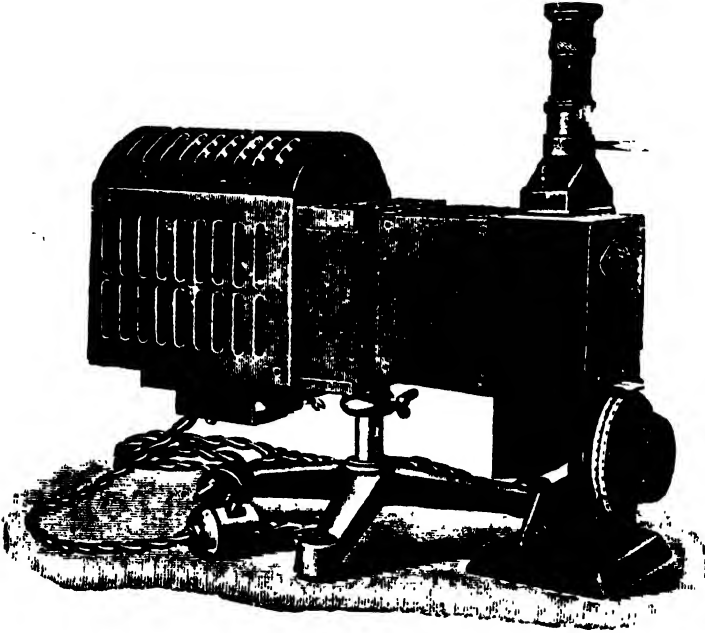
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